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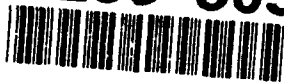
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The piezoelectric strain constant,  $d_{31}$ , stress constant,  $e_{31}$ , and electro-mechanical coupling coefficients,  $k_{31}$ , of Nylon-11 and Nylon-7 films were measured up to a temperature close to their melting points. They were found to exhibit their highest values and, in addition, excellent thermal stability at temperatures between 100°C and 200°C. Maximum stable values were  $d_{31} = 14$  pC/N and  $e_{31} = 21$  mC/m<sup>2</sup> for Nylon-11, and  $d_{31} = 17$  pC/N and  $e_{31} = 27$  mC/m<sup>2</sup> for Nylon-7. Corresponding values of  $k_{31}$  were 0.049 and 0.054. Poled and then

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annealed Nylon samples exhibit little decay of these values even after annealing at 185°C and 200°C for Nylon-11 and Nylon-7, respectively, while poly(vinylidene fluoride) samples showed a large decay in response, decreasing to 4.9 pC/N, 11 mC/m, and  $k = 0.019$  after annealing at 175°C. The extraordinary stability of the piezoelectric activity of these Nylon samples was considered to be related to ferroelectric reorientation of the amide groups dipoles followed by closer packing of the hydrogen bonded sheet structure in the crystalline regions after the annealing treatment.

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**Prepared for Publication in  
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# High Temperature Characteristics of Nylon-11 and Nylon-7 Piezoelectrics

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ABSTRACT: The piezoelectric strain constant,  $d_{31}$ , stress constant,  $e_{31}$ , and electromechanical coupling coefficients,  $k_{31}$ , of Nylon-11 and Nylon-7 films were measured up to a temperature close to their melting points. They were found to exhibit their highest values and, in addition, excellent thermal stability at temperatures between 100°C and 200°C. Maximum stable values were  $d_{31} = 14$  pC/N and  $e_{31} = 21$  mC/m<sup>2</sup> for Nylon-11, and  $d_{31} = 17$  pC/N and  $e_{31} = 27$  mC/m<sup>2</sup> for Nylon-7. Corresponding values of  $k_{31}$  were 0.049 and 0.054. Poled and then annealed Nylon samples exhibit little decay of these values even after annealing at 185°C and 200°C for Nylon-11 and Nylon-7, respectively, while poly(vinylidene fluoride) samples showed a large decay in response, decreasing to 4.9 pC/N, 11 mC/m<sup>2</sup>, and  $k_{31} = 0.019$  after annealing at 175°C. The extraordinary stability of the piezoelectric activity of these Nylon samples was considered to be related to ferroelectric reorientation of the amide groups dipoles followed by closer packing of the hydrogen bonded sheet structure in the crystalline regions after the annealing treatment.

## Introduction

Compared with the large number of studies of Nylons in terms of their molecular structure and elastic characteristics, studies of the piezoelectric characteristics of Nylons have been confined to restricted groups of researchers.<sup>1-9</sup> The first significant piezoelectric response (piezoelectric strain constant  $d_{31} = 3.0$  pC/N) of a poled Nylon-11 film was reported by Newman et al. in 1980.<sup>2</sup> Recently, our laboratory has been studying the piezoelectric and ferroelectric characteristics of odd Nylons. Scheinbeim<sup>3</sup> reported that the piezoelectric response of poled, melt quenched, Nylon-11 films continued to increase rapidly with increasing temperature to a value of about 12 pC/N at the maximum measurement temperature of 107°C. Mathur et al.<sup>5</sup> reported that the piezoelectric stress and strain constants ( $e_{31}$  and  $d_{31}$ ) showed hysteresis-like loops when uniaxially oriented Nylon-11 films were polarized under a series of positive and negative poling fields. In addition, studies of Nylon-11 films crystallized from solution under high electric fields showed  $d_{31}$  values of 7.1 pC/N at room temperature.<sup>6</sup> Wu et al.<sup>7</sup> studied the piezoelectric response of poled Nylon-9 and Nylon-11 films. More recently, we discovered that melt quenched and cold drawn Nylon-11 films with three dimensional order exhibit clear ferroelectric behavior in D-E (electric displacement versus electric field) hysteresis studies.<sup>8,9</sup>

As far as the ferroelectric behavior and remanent polarization are concerned, Nylon-11 and Nylon-7 show comparable properties with those of poly(vinylidene fluoride) (PVF<sub>2</sub>). The ques-

tion arises as to why the piezoelectric constants of these odd Nylons are small compared with those of PVF<sub>2</sub>. To answer this question, it is important to note the large difference in their glass transition temperatures,  $T_g$ . The values of  $T_g$  were reported to be 68°C<sup>10</sup> and about -50°C<sup>11,12</sup> for Nylon-11 and PVF<sub>2</sub>, respectively. If we compare piezoelectric constants at room temperature, we find that this is about 50°C below and 70°C above  $T_g$  for Nylon-11 and PVF<sub>2</sub>, respectively. It should be noted that  $d_{31}$  for PVF<sub>2</sub> at a temperature of -100°C (that is about 45°C below the glass transition temperature) is only  $\approx 1.7$  pC/N, so that the values of  $d_{31}$  for Nylon-11 and Nylon-7 at comparable temperatures with respect to the glass transition temperature is actually quite high. It is therefore necessary to obtain the piezoelectric constant data above  $T_g$  for the odd Nylons in order to compare them to PVF<sub>2</sub>. We note that the piezoelectric constants,  $d_{31}$  and  $e_{31}$ , and dielectric constant rapidly increase with increasing temperature above  $T_g$ .<sup>3,7</sup> It is also well known that the dielectric constant steeply increases above  $T_g$  at higher temperatures due to ionic conduction. In fact, above the glass transition temperature, the ionic conduction in the Nylons becomes so large that the automatic measurement system used stopped due to charge amplifier saturation caused by the large D. C. offset current. In manual operation, the measurement also became impossible for the same reason. We tried several methods for performing the measurements above the glass transition temperature of the odd Nylons. Finally, we employed three simple and adequate methods; field sweeping of the mobile ionic species, use of a D. C. blocking

capacitor to the input of the charge amplifier, and use of higher frequency measurements. We were then able to measure the piezoelectric constants of Nylon-11 and Nylon-7 up to a temperature close to their melting points ( $T_m \approx 195^\circ\text{C}$  for Nylon-11 and  $T_m \approx 235^\circ\text{C}$  for Nylon-7).

The present study demonstrates the excellent high temperature characteristics of the piezoelectric response ( $d_{31}$  and  $e_{31}$ ) of Nylon-11 and Nylon-7 film samples compared with those of PVF<sub>2</sub> which were also measured up to the melting point. In addition to the piezoelectric characteristics, the temperature dependences of the modulus and dielectric constant were also measured.

## Experimental Section

The Nylon films used in this study were prepared by melting the Nylon powder between aluminum foils in a hot press at  $210^\circ\text{C}$  and  $240^\circ\text{C}$  for Nylon-11 and Nylon-7, respectively. Then, the molten films were quenched by placing them into an ice bath. The quenched films were then uniaxially stretched to a draw ratio of 3:1 at room temperature. The final film thickness of the sample was 10 - 30  $\mu\text{m}$ .

Gold electrodes (area of 12 - 24  $\text{mm}^2$ ) were evaporated on opposing surfaces of the film after stretching. The evaporation process was carried out carefully in order to avoid heating (annealing) the samples.

Poling of samples was carried out at room temperature by applying a triangular shaped electric field pulse, with a maximum

amplitude of 200 MV/m, to the samples, so as to determine their D versus E characteristics. The samples were placed in a silicone oil bath for these measurements and the period of the triangular voltage waveform was 1000 s. Before the poling procedure, the samples were pretreated by applying a static electric field of 150 - 180 MV/m for a few hours for the purpose of field-sweeping out most of the mobile ionic species.

The dielectric constant,  $\epsilon$ , piezoelectric strain constant,  $d_{31}$ , piezoelectric stress constant,  $e_{31}$ , and the elastic modulus,  $c$ , were measured at 104 Hz using a Rheolograph Solid (Toyoseiki). At higher frequencies, the dielectric constant,  $\epsilon$ , was measured using an impedance analyzer (HP 4192A) at 1, 10 and 100 kHz.

Operation of various functions in the system was consigned to a microcomputer.

## Results and Discussion

**1. D - E Hysteresis Characteristics** Figures 1(a) and (b) show the current density,  $J$ , and electric displacement,  $D$ , as a function of electric field, respectively, for three kinds of samples; Nylon-11, Nylon-7 and PVF<sub>2</sub>. These measurements were performed at room temperature. The Nylon samples exhibit a much higher current density peak at the coercive field than PVF<sub>2</sub>. The remanent polarization,  $P_r$ , of the present samples were 58, 93 and 55 mC/m<sup>2</sup>, and the coercive fields,  $E_c$ , were 56, 92 and 46 MV/m for Nylon-11, Nylon-7 and PVF<sub>2</sub> samples, respectively.

From the unit cell parameters<sup>13-15</sup> and the value<sup>1,16</sup> of the



dipole moment of the amide group (about  $1.24 \times 10^{-29}$  C.m) and the  $-\text{CF}_2-\text{CH}_2-$  unit ( $7 \times 10^{-30}$  C.m), we estimated the spontaneous polarization of Nylon-11, Nylon-7 and  $\text{PVF}_2$  crystals to be 48, 73 and  $132 \text{ mC/m}^2$ , respectively. The measured values of  $P_r$  for the Nylon samples were larger than these values. This is considered to be related to the nature of semicrystalline polymers. The measured bulk remanent polarization may be estimated as  $P_r = f L P_s$ ,<sup>17</sup> where  $f$  is the portion of reorientable dipoles and  $L$  is given as  $3\epsilon / (2\epsilon + \epsilon_c)$ , which is applicable to a two-phase model consisting of spherical crystals with dielectric constant  $\epsilon_c$ , distributed in an amorphous matrix with dielectric constant  $\epsilon$ . The present Nylon samples usually showed significant high field D. C. conduction at room temperature. The D-E hysteresis measurements were carried out at a very low frequency; 1 MHz. Therefore, the value of  $\epsilon$  is much larger than  $\epsilon_c$  resulting in  $L \approx 1.5$ . In this case, the measured remanent polarization is expected to be  $72 \text{ mC/m}^2$  for Nylon-11 and  $110 \text{ mC/m}^2$  for Nylon-7. The  $\text{PVF}_2$  used was a capacitor grade film and showed no obvious D. C. conduction at room temperature. For  $\text{PVF}_2$ , we obtain the value  $L = 1.34$  by using  $\epsilon = 14$  and  $\epsilon_c = 3.3$ . We can estimate, approximately, that 81%, 85% and 31% of the dipoles are reoriented by the external electric field for Nylon-11, Nylon-7 and  $\text{PVF}_2$ , respectively. It is obvious from this analysis that the Nylon samples give rise to much larger degrees of dipole orientation than  $\text{PVF}_2$  samples when poled at room temperature.

**2. Modulus and Dielectric Constant** Since piezoelectricity is a property resulting from a combination of the electrical and

mechanical characteristics of a material, it is important to measure both mechanical modulus and dielectric constant. Figure 2 shows the temperature dependence of the modulus (real part  $c'$  and imaginary part  $c''$ ) for samples of Nylon-11 and Nylon-7. The measurement frequency was 104 Hz. The Nylon samples exhibit three noticeable relaxation processes. The high temperature relaxation appears at 80 - 100°C and is commonly designated the  $\alpha$  relaxation. As the temperature decreases, the  $\beta$  relaxation appears at -55°C for Nylon-11 and at -33°C for Nylon-7, and, finally, the  $\gamma$  relaxation appears at -156°C for Nylon-11 and -143°C for Nylon-7.

Figure 3 shows a logarithmic plot of the dielectric constant,  $\epsilon$ , as a function of temperature for Nylon-11 measured at frequencies of 1 kHz, 10 kHz and 100 kHz. A similar plot for Nylon-7 is shown in Figure 4. The dielectric constant also exhibits three relaxation processes, the  $\alpha$ ,  $\beta$  and  $\gamma$  relaxations. However, there is a significant difference in the relaxation behavior comparing the modulus and the dielectric constant. The modulus exhibits two strong relaxations, the  $\alpha$  and the  $\gamma$  relaxations. The  $\gamma$  relaxation is much stronger than the  $\alpha$  relaxation, while the dielectric constant exhibits a stronger  $\alpha$  relaxation and a weaker  $\gamma$  relaxation. Although the  $\alpha$  relaxation in Nylons has normally been designated as the glass transition temperature,  $T_g$ , some questions<sup>10</sup> were posed about this designation due to the very strong  $\gamma$  relaxation. The modulus and dielectric constant data obtained provide convincing evidence for the mechanisms involved. As the temperature gradually increases, the micro-brownian motion of hydrocarbon sections of the Nylons is excited

in the noncrystalline regions, while the amide groups stay as unexcited states, probably due to hydrogen bonding. The hydrocarbon sections of Nylon-11 and Nylon-7 are much longer than the amide group and only the amide group has a strong dipole moment. As a result, the strong and glass-transition-like  $\gamma$  relaxation appears only in the modulus data. In fact, the  $\gamma$  relaxation in Nylons also obeys the WLF relation.<sup>10</sup> As the temperature increases further, some hydrogen bonds will break and longer chain segments, including both amide groups and hydrocarbon sections, begin micro-brownian motion in the noncrystalline regions. The  $\alpha$  relaxation also obeys the WLF relation<sup>10</sup> and can be designated as the glass transition process.

On the other hand, it is well known that PVF<sub>2</sub> films with form-I crystals do not show a noticeable  $\alpha$  relaxation but exhibit a strong  $\beta$  relaxation around -40°C followed by a  $\gamma$  relaxation. Only the  $\beta$  relaxation is very strong and appears in both the elastic modulus and dielectric constant data and this relaxation is commonly designated as the glass transition temperature of PVF<sub>2</sub>. PVF<sub>2</sub> has a dipole moment in the small -CF<sub>2</sub>-CH<sub>2</sub>- monomer unit and, as a result, segmental chain motion cannot occur without dipole motion. This structural difference gives a qualitative difference to the elastic modulus characteristics for Nylons and PVF<sub>2</sub>; Nylons exhibit two steps related to the onset of micro-brownian motions in molecular chains, while PVF<sub>2</sub> exhibits only one step. On the other hand, the behavior of the dielectric constant is essentially the same for Nylon and PVF<sub>2</sub>. From this understanding of the response of the dipoles in Nylon and PVF<sub>2</sub>, we expect that if the response of the dipoles to an electrical

excitation is essentially the same in both Nylon and  $\text{PVF}_2$ , the response to the mechanical excitation (piezoelectric effect) may also be the same. It is also important to remember that the Nylons studied have much higher  $T_g$ 's than that of  $\text{PVF}_2$  (about a  $120^\circ\text{C}$  difference), and that the Nylons do not show a dielectric anomaly, which would indicate a Curie transition, until they melt. These two features of Nylons may be important in terms of high temperature piezoelectric applications.

**3. Piezoelectric Constants** Once we observed the superior D-E hysteresis characteristics of the Nylon samples and also, essentially, the same type of dielectric response of Nylons as that of  $\text{PVF}_2$ , we expected reasonably high piezoelectric activities for the Nylon samples above  $T_g$ . In Figure 5, we show the piezoelectric strain constant,  $d'_{31}$ , and in Figure 6 the piezoelectric stress constant,  $e'_{31}$ , versus temperature for Nylon-11, Nylon-7 and  $\text{PVF}_2$  measured at 104 Hz from  $50^\circ\text{C}$  up to temperatures close to their melting points. The stable values of the piezoelectric constants presented here occur after annealing the poled samples at  $185^\circ\text{C}$  for Nylon-11 and at  $200^\circ\text{C}$  for Nylon-7 for two hours, and after measurements up to  $175^\circ\text{C}$  for  $\text{PVF}_2$ . The signs of  $d'_{31}$  and  $e'_{31}$  of the Nylon samples were the same as those of  $\text{PVF}_2$ ; positive. Both the  $d'_{31}$  versus  $T$  and  $e'_{31}$  versus  $T$  curves of the Nylons exhibit large increases around the glass transition temperature. Both curves show a shoulder between  $120^\circ\text{C}$  and  $140^\circ\text{C}$  and exhibit a tendency to saturate. The maximum values of  $d'_{31}$  for Nylon-11 and Nylon-7 are 14 and 17 pC/N, respectively, and the

maximum values of  $e'_{31}$  for Nylon-11 and Nylon-7 are 21 and 27 mC/m<sup>2</sup>, respectively. On the other hand, the PVF<sub>2</sub> sample exhibits an almost constant  $d'_{31}$  and an almost linearly decreasing curve for  $e'_{31}$  with increasing temperature. The values of  $d'_{31}$  and  $e'_{31}$  for PVF<sub>2</sub> at high temperatures, for example at 100°C, are 5 pC/N and 7 mC/m<sup>2</sup>, respectively. PVF<sub>2</sub> of course never reaches the highest temperatures, since it melts around 175°C. It is obvious that the high temperature piezoelectric characteristics of these Nylons are better than those of PVF<sub>2</sub>. To our knowledge, no other polymeric material exhibits useful values of  $d'_{31}$  and  $e'_{31}$  at these high temperatures.

To understand the present data, it is necessary to remember that we added a D. C. blocking capacitor to the input of the charge amplifier to prevent saturation while obtaining the high temperature data. The maximums value of the real part and imaginary part of the dielectric constant of the Nylon-11 sample were  $\epsilon' = 1014$  and  $\epsilon'' = 1894$  at 187°C, and of the Nylon-7 sample were  $\epsilon' = 401$  and  $\epsilon'' = 1566$  at 200°C. At these temperatures, the impedance becomes 51.9 k $\Omega$  and 118 k $\Omega$  for the Nylon-11 and Nylon-7 samples, respectively. We used a capacitance of 2.2  $\mu$ F, whose impedance is much smaller (696  $\Omega$  at 104 Hz) than the sample impedance. We found, however, that this large capacitance also passed D. C. drift noise, which is randomly distributed over some very low frequency region and sometimes large enough in amplitude to cause the charge amplifier to saturate. We selected the capacitance to be between 0.15  $\mu$ F and 2.2  $\mu$ F depending on the sample impedance. The major side effect of the D. C. blocking capacitor was a significant change in the value of the imaginary part of

the piezoelectric constants above  $\approx 160^{\circ}\text{C}$  or  $\approx 180^{\circ}\text{C}$  for Nylon-11 and Nylon-7, respectively. These data were considered unreliable and are not presented.

**4. Annealing Effects on the Piezoelectric Properties** In a previous study<sup>9</sup> we reported the effect of annealing on the ferroelectric behavior of Nylon-11 and Nylon-7. We pointed out that quenched and then cold drawn and annealed Nylon-11 and Nylon-7 films show clear ferroelectric behavior at annealing temperatures below about  $70^{\circ}\text{C}$  for Nylon-11 and below about  $115^{\circ}\text{C}$  for Nylon-7. When the Nylon samples were exposed to a temperature above the glass transition, the ferroelectric behavior significantly decreased.

Figures 7 - 9 show the effect of annealing after poling on the  $d_{31}$  versus  $T$  characteristics of Nylon-11, Nylon-7 and  $\text{PVF}_2$  samples, respectively. The measurement frequency was 104 Hz. The curves labeled "unannealed" indicate characteristics of the first measurement after poling. The curves labeled "annealed" indicate characteristics measured after annealing of the poled samples. The annealing temperatures of the Nylon-11 and Nylon-7 samples were  $185^{\circ}\text{C}$  and  $200^{\circ}\text{C}$ , respectively, and the annealing time was two hours. For the  $\text{PVF}_2$  samples, four characteristics are presented: Curve (1) represents the first run of the unannealed sample, curve (2) the second run after the first measurement, curve (3) the third run after annealing at  $120^{\circ}\text{C}$  for 17 hours, and curve (4) the forth run after the measurement up to  $175^{\circ}\text{C}$ .

Figures 10 - 12 show the annealing effect after poling on

the  $\epsilon_{31}$  versus  $T$  characteristics of Nylon-11, Nylon-7 and PVF<sub>2</sub> samples, respectively. The labeling of the curves is similar to those used in Figures 7 - 9. Even for PVF<sub>2</sub>, piezoelectric measurements at temperatures above  $\approx 120^\circ\text{C}$  is difficult to obtain and no data has been published. We performed the measurements carefully by using a manual (as opposed to automatic) mode of the equipment. The continuous lines represent data obtained using the automatic mode and the explicit data points represent data obtained using the manual mode.

Both the Nylon and PVF<sub>2</sub> samples reveal certain characteristic changes in the curves after annealing. However, we can easily notice that there is a significant difference in the annealing behavior comparing Nylon-11 and Nylon-7 with PVF<sub>2</sub>. Change in the  $d'_{31}$  vs  $T$  and  $e'_{31}$  versus  $T$  curves of Nylon appears only in the temperature region above the glass transition temperature, while the changes in the case of PVF<sub>2</sub> is an irreversible overall decrease in the measured temperature region. This difference leads us to one important conclusion. Poled then annealed Nylon films do not suffer from dipolar randomization even at high temperatures close to the melting point.

Each  $d'_{31}$  versus  $T$  and  $e'_{31}$  versus  $T$  curve for the unannealed Nylons exhibits a convex shape with a single peak. The maximum value of  $d'_{31}$  is 21 pC/N at  $163^\circ\text{C}$  for Nylon-11 and 30 pC/N at  $180^\circ\text{C}$  for Nylon-7, and the maximum value of  $e'_{31}$  is 26 mC/m<sup>2</sup> at  $150^\circ\text{C}$  for Nylon-11 and 34 mC/m<sup>2</sup> at  $168^\circ\text{C}$  for Nylon-7. After annealing, the curve shows a plateau with an almost constant value of  $d'_{31} = 14$  pC/N for Nylon-11,  $d'_{31} = 17$  pC/N for Nylon-7, and  $e'_{31} = 21$  mC/m<sup>2</sup> for Nylon-11 and  $e'_{31} = 26$  mC/m<sup>2</sup> for

Nylon-7. After annealing, the values of  $d'_{31}$  and  $e'_{31}$  decrease to about 65 - 75% of the initial maximum value. However, both  $d'_{31}$  and  $e'_{31}$  begin to show less temperature dependence and do not show further decrease even after several exposures at a high temperature close to the melting point.

The PVF<sub>2</sub> sample, on the other hand, exhibits much poorer thermal stability for  $d'_{31}$  and  $e'_{31}$ . The unannealed sample shows convex shaped  $d'_{31}$  versus T and  $e'_{31}$  versus T curves similar to Nylon-11 and Nylon-7. The maximum values are as high as 26 pC/N at 26°C and 77 mC/m<sup>2</sup> at 35°C. However this piezoelectric response significantly decreases after annealing. The maximum value of  $d'_{31}$  decreases to 8.1 pC/N (31%) after annealing at 120°C and to 4.9 pC/N (19%) after measurement up to 175°C. Similarly, the maximum value of  $e'_{31}$  decreases to 20 mC/m<sup>2</sup> (26%) and to 11 mC/m<sup>2</sup> (15%) after exposure to temperatures of 120°C and 175°C, respectively. As expected, PVF<sub>2</sub> also exhibits this significant decrease in piezoelectric response even at temperatures lower than T<sub>g</sub>. For example, at -100°C, the initial value of  $d'_{31}$  was 1.7 pC/N and of  $e'_{31}$  was 27 mC/m<sup>2</sup>. This decreases to 0.35 pC/N (21%) and 8.1 mC/m<sup>2</sup> (30%) after annealing at 120°C, and 0.23 pC/N (14%) and 5.1 mC/m<sup>2</sup> (19%) after the measurement up to 175°C.

The measured piezoelectric constants have been considered to be proportional to the remanent polarization and also be a function of Poisson's ratio and the electrostriction constant of the sample.<sup>17</sup> The large increase in the piezoelectric constants,  $d'_{31}$  and  $e'_{31}$ , above the glass transition temperature of highly stretched PVF<sub>2</sub> films have been explained in terms of the change



in Poisson's ratio.<sup>18</sup> In temperature regions lower than  $T_g$ , the measured piezoelectric constants begin to show a "pure" piezoelectric effect. The present experiments revealed that the piezoelectric constants,  $d'_{31}$  and  $e'_{31}$ , of Nylon samples exhibit essentially a similar temperature dependence to that of  $PVF_2$ . Since the measured piezoelectric constants are proportional to remanent polarization regardless of temperature, it is easy to conclude that the observed large decrease in the piezoelectric constants of  $PVF_2$  is due to significant loss of dipole orientation which was initially induced by poling. On the other hand, the decrease in the piezoelectric constants of the Nylon samples observed only in the temperature region above  $T_g$  may be ascribed to changes in the dimensional effect (Poisson's ratio) caused by crystallographic and morphological changes produced by annealing. The lack of any observed changes in the piezoelectric constants in the temperature region below  $T_g$  after high temperature annealing indicates, essentially, that no loss of dipole orientation occurs as a result of the annealing process.

The large difference observed in the annealing effect between Nylons and  $PVF_2$  originates in the difference in molecular structures between Nylon and  $PVF_2$ . In a previous X-ray study,<sup>19</sup> it was pointed out that quenched then cold drawn Nylon films had three dimensional molecular order; the hydrogen bonded sheet structure was parallel to the film surface with the chains in the draw direction. During poling, these hydrogen bonded sheets rearrange and reform with the hydrogen bonded sheets perpendicular to the film surface with the dipoles aligned along the applied electric field direction. Similar to the conclusions of the

previous study, the effects of annealing in these Nylons can be interpreted in terms of a rearrangement of the hydrogen bonded sheet structure, i. e. a significant decrease in spacing between the hydrogen bonded sheets after annealing which results in an increased difficulty for the amide groups to reorient with increasing thermal motion. Structural studies of this behavior using X-ray diffraction and IR absorbance measurements will be published separately.

**5. Anisotropy of Drawn Nylon films** The Nylon film samples studied were highly stretched and we expected a certain degree of anisotropy with respect to the modulus and piezoelectric constants. Figure 13 shows the temperature dependence of the elastic modulus along the draw direction,  $c_{11}$ , and perpendicular to the draw direction,  $c_{22}$  measured at 10 Hz. The value of  $c'_{22}$  is about 35 to 40% of that of  $c'_{11}$  over the temperature region from  $-196^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , exhibiting the high anisotropy of the sample (for example, at  $-150^{\circ}\text{C}$ ,  $c'_{11} \approx 14.3$  GPa, while  $c'_{22} \approx 5.8$  GPa). According to a study of drawing procedures of polymers by Peterlin et al.,<sup>20</sup> the transformation from lamellae to microfibrils is complete at a draw ratio between 2 and 3 in Nylon 6 or 66, while between 8 and 10 in linear polyethylene. We can expect, therefore, that our Nylon samples have almost completed the transformation and consist primarily of microfibrils.

Also related to this high anisotropy, we noticed some interesting properties of the Nylon samples. The films easily break when stress is applied perpendicular to the draw direction. As we

see on the  $c_{22}$  vs  $T$  curve in Figure 13, the curves are not continuous. This is because of fracture of the samples during measurement. In addition, when the stretched films were annealed, they did not shrink in the draw direction but rather showed a small extension. This is quite different from the behavior of drawn PVF<sub>2</sub> (draw ratio of about 5:1), which showed considerable shrinkage in the draw direction during annealing.

It may also be interesting to observe any anisotropy in the piezoelectric constants of the stretched Nylon films. Figure 14 shows the temperature dependence of the piezoelectric strain constants,  $d_{31}$  and  $d_{32}$  of Nylon-11 measured at 10 Hz. The sign of  $d'_{32}$  was positive. It is of particular interest that the value of  $d'_{32}$  is significantly larger than that of  $d'_{31}$  in the temperature region below  $T_g$ . For example at  $-100^\circ\text{C}$ ,  $d'_{32} = 2.3$  pC/N, while  $d'_{31} = 0.36$  pC/N. The discontinuity in the curve of  $d_{32}$  is due to the fracture of the sample during the measurement.

Figure 15 shows the temperature dependence of the piezoelectric stress constants,  $e_{31}$  and  $e_{32}$  of Nylon-11 measured at 10 Hz. The value of  $e'_{32}$  is much larger than the value of  $e'_{31}$  below a temperature of about  $50^\circ\text{C}$ . The sign of  $e'_{32}$  was also positive. The  $e'_{32}$  value exhibit less of a temperature dependence than the values of  $e'_{31}$  and the maximum value is about  $8.6$  mC/m<sup>2</sup> at about  $-70^\circ\text{C}$ .

It should be noted that the values of  $d'_{32}$  and  $e'_{32}$  of Nylon-11 in the low temperature region are much larger than the stable value of  $d'_{31}$  and  $e'_{31}$  of PVF<sub>2</sub>. For example, at  $-100^\circ\text{C}$ ,  $d'_{32} = 2.3$  pC/N and  $e'_{32} = 8.5$  mC/m<sup>2</sup> for Nylon-11, while  $d'_{31} = 0.23$  pC/N and  $e'_{31} = 5.1$  mC/m<sup>2</sup> for PVF<sub>2</sub>. The value of  $d'_{32}$

and  $e'_{32}$  have been reported to be much smaller than  $d'_{31}$  and  $e'_{31}$  for PVF<sub>2</sub>.<sup>21</sup>

**6. Electromechanical Coupling Constant** The electromechanical coupling coefficient,  $k_{31}$  of the present Nylon samples was obtained by using the relation

$$k_{31} = d_{31} (c/\epsilon_0\epsilon)^{\frac{1}{2}}, \quad (1)$$

where  $\epsilon_0$  is the free space permittivity. Figure 16 shows the coupling coefficient,  $k_{31}$ , as a function of temperature for the annealed samples of Nylon-11, Nylon-7 and PVF<sub>2</sub>. The value is obtained by using the measured quantities most of which are shown in Figures 5 and 9. The measurement frequency is 104 Hz. This frequency is low enough to regard the value of  $k_{31}$  as the static value except in the high temperature region for the Nylons.

Annealing effects on the coupling coefficients of Nylons and PVF<sub>2</sub> are very similar to those of the piezoelectric constants discussed in Section 4: Change in the coupling coefficient of Nylon appears only in the temperature region above the glass transition temperature, while that of PVF<sub>2</sub> is an overall decrease in the measured temperature region (The maximum value of  $k_{31}$  for unannealed PVF<sub>2</sub> is about 0.12). It is interesting to note that the values of  $k_{31}$  for both Nylon-11 and Nylon-7 become larger than that of PVF<sub>2</sub> in the low temperature region below about -50°C after the annealing of PVF<sub>2</sub> at 175°C; for example  $k_{31} = 0.02$  for both Nylons and  $k_{31} = 0.008$  for PVF<sub>2</sub>. At higher temperatures above the glass transition temperature, the values of  $k_{31}$  of

Nylons are larger than those of  $\text{PVF}_2$ . However, they sharply decrease as the temperature increases. This is obviously due to the enormous increase in dielectric constant of the Nylon samples. Since this increase is known to be associated with the response of mobile ionic species, the sharp decrease in  $k_{31}$  should not be regarded as an intrinsic phenomenon.

In order to obtain intrinsic values for the coupling coefficient, it is necessary to obtain a dielectric constant which is independent of ionic response. To perform this procedure, we measured the frequency dependence of the dielectric constant at many temperatures and tried a Cole-Cole plot of the data. Figures 17 - 19 show the frequency dependence of the dielectric constant at the indicated temperatures for the poled and annealed Nylon-11, Nylon-7 and  $\text{PVF}_2$  samples, respectively. Above the glass transition temperature, the Nylon samples show characteristic increases in both  $\epsilon'$  and  $\epsilon''$  as the frequency decreases. These increases make it difficult to determine the intrinsic static value of dielectric constant above  $T_g$ .

Figure 20 (a), (b), and (c) show the Cole-Cole plot of the dielectric data for Nylon-11, Nylon-7 and  $\text{PVF}_2$ , respectively. Measured data for the three samples follow the expected Cole-Cole arc except at the very high and the very low frequency regions. In the Cole-Cole plot, the curvature of the  $\epsilon''$  versus  $\epsilon'$  curve changes to the opposite sign when the ionic contribution dominates. This qualitative change makes it easy to distinguish the intrinsic dielectric constant from the ionic contribution. The extrapolation of the data by using an arc determines both the static value,  $\epsilon'_s$ , and the instantaneous value,  $\epsilon'_\infty$ , of the

dielectric constant. The values of  $\epsilon'_0$  for Nylon-11, Nylon-7, and PVF<sub>2</sub> are 3.15, 3.35, and 3.25, respectively, almost the same within experimental error. The value of  $\epsilon'_s$  at the highest temperatures for Nylon-11, Nylon-7, and PVF<sub>2</sub> are about 18, 16, and 15, respectively. It is interesting to note that these values are very similar for Nylon and PVF<sub>2</sub>, although the experimental error may be significant for the Nylon samples.

Figure 21 shows the intrinsic static values of the coupling coefficient of Nylon-11, Nylon-7 and PVF<sub>2</sub> samples determined by using the static dielectric constants and Eq. (1). The  $d_{31}$  data used are presented in Figure 5. These are the stable values obtained after annealing. Similar to the piezoelectric data shown in Figs. 5 and 6, at high temperatures (above  $\approx 70^\circ\text{C}$ ), the intrinsic coupling coefficient values for Nylon-11 and Nylon-7 are higher than values obtained for annealed PVF<sub>2</sub>. For example, the maximum values of  $k_{31}$  are 0.049, 0.054, and 0.019 for Nylon-11, Nylon-7 and PVF<sub>2</sub> samples, respectively. The Nylon-7 sample shows a flat response with temperature with a  $k_{31}$  value of  $\approx 52\%$ , from about  $120^\circ\text{C}$  up to  $200^\circ\text{C}$ .

## Conclusions

The variation in piezoelectric response of Nylon-11 and Nylon-7 with temperature has been explored and compared with PVF<sub>2</sub>, to provide insight into the role of elastic and dielectric relaxation on piezoelectricity and on the thermal stability of piezoelectricity.

Nylon-11 and Nylon-7 films exhibit the highest values of piezoelectric strain coefficient,  $d_{31}$ , stress coefficient,  $e_{31}$ , and electromechanical coupling coefficient,  $k_{31}$ , together with excellent thermal stability at temperatures between 100°C and 200°C. Maximum stable values obtained were  $d_{31} = 14$  pC/N,  $e_{31} = 21$  mC/m<sup>2</sup> and  $k_{31} = 0.049$  for Nylon-11, and  $d_{31} = 17$  pC/N,  $e_{31} = 27$  mC/m<sup>2</sup> and  $k_{31} = 0.054$  for Nylon-7. Poled and then annealed Nylon samples exhibit little decay of these values even after annealing at 185°C and 200°C for Nylon-11 and Nylon-7, respectively for two hours. The extraordinary stability of the piezoelectric activity of the Nylon samples is considered to be related to the ferroelectric reorientation of the amide group dipoles followed by closer packing of the hydrogen bonded sheets in the crystalline regions after the poling and annealing procedures. In the low temperature region below about -50°C, the Nylons exhibit higher values of  $d_{32}$ ,  $e_{32}$  and  $k_{31}$  than the  $d_{31}$ ,  $e_{31}$  and  $k_{31}$  values of PVF<sub>2</sub>.

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## Figure captions

**Figure 1.** (a) Current density versus electric field and (b) electric displacement versus electric field for three kinds of samples: Nylon-11, Nylon-7 and PVF<sub>2</sub> films. These characteristics were measured at room temperature.

**Figure 2.** Temperature dependence of the modulus (real part  $c'$  and imaginary part  $c''$ ) for samples of Nylon-11 and Nylon-7 measured at 104 Hz.

**Figure 3.** Logarithmic plot of dielectric constant as a function of temperature for Nylon-11 measured at frequencies of 1 kHz, 10 kHz and 100 kHz.

**Figure 4.** Logarithmic plot of dielectric constant as a function of temperature for Nylon-7 measured at frequencies of 1 kHz, 10 kHz and 100 kHz.

**Figure 5.** Piezoelectric strain constant,  $d'_{31}$ , for Nylon-11, Nylon-7 and PVF<sub>2</sub> samples measured at 104 Hz from 50°C up to temperatures close to their melting points. Stable values are shown after annealing the poled samples at 185°C for Nylon-11 and at 200°C for Nylon-7 for 2 h, and after measurement up to 175°C for PVF<sub>2</sub>.

**Figure 6.** Piezoelectric stress constant,  $e'_{31}$ , for samples of Nylon-11, Nylon-7 and PVF<sub>2</sub> measured at 104 Hz. Stable values are shown similar to those of Figure 5.

**Figure 7.** Annealing effects after poling on the  $d_{31}$  versus T characteristics of Nylon-11. The measurement frequency was 104 Hz, and the annealing temperature and time were 185°C and 2 h.

**Figure 8.** Annealing effect (after poling) on the  $d_{31}$  versus T characteristics of Nylon-7. The measurement frequency was 104 Hz, and the annealing temperature and time were 200°C and 2 h.

**Figure 9.** Annealing effect (after poling) on the  $d_{31}$  versus T characteristics of PVF<sub>2</sub>. Curve (1) represents the first run of an unannealed sample, curve (2) the second run after the first measurement, curve (3) the third run after annealing at 120°C for 17 hours, and curve (4) the fourth run after the measurement up to 175°C. The measurement frequency was 104 Hz.

**Figure 10.** Annealing effect (after poling) on the  $e_{31}$  versus T characteristics of Nylon-11. The measurement frequency was 104 Hz, and the annealing temperature and time were 185°C and 2 h.

**Figure 11.** Annealing effect (after poling) on the  $e_{31}$  versus T characteristics of Nylon-7. The measurement frequency was 104 Hz, and the annealing temperature and time were 200°C and 2 h.

**Figure 12.** Annealing effect after poling on the  $e_{31}$  versus  $T$  characteristics of  $\text{PVF}_2$ . Curve (1) represents the first run of the unannealed sample, curve (2) the second run after the first measurement, curve (3) the third run after annealing at  $120^\circ\text{C}$  for 17 hours, and curve (4) the fourth run after the measurement up to  $175^\circ\text{C}$ . The measurement frequency was 104 Hz.

**Figure 13.** Temperature dependence of the elastic modulus along the draw direction,  $c_{11}$ , and perpendicular to the draw direction,  $c_{22}$  of Nylon-11 measured at 10 Hz.

**Figure 14.** Temperature dependence of the piezoelectric strain constants,  $d_{31}$  and  $d_{32}$  of Nylon-11 measured at 10 Hz.

**Figure 15.** Temperature dependence of the piezoelectric stress constants,  $e_{31}$  and  $e_{32}$  of Nylon-11 measured at 10 Hz

**Figure 16.** Electromechanical coupling coefficient,  $k_{31}$ , as a function of temperature for the annealed samples of Nylon-11, Nylon-7 and  $\text{PVF}_2$ . The measurement frequency was 104 Hz.

**Figure 17.** Frequency dependence of the dielectric constant at indicated temperatures for poled and annealed Nylon-11.

**Figure 18.** Frequency dependence of dielectric constants at indicated temperatures for poled and annealed Nylon-7.

**Figure 19.** Frequency dependence of the dielectric constant at indicated temperatures for poled and annealed PVF<sub>2</sub>.

**Figure 20.** (a), (b), and (c) show a Cole-Cole plot of the dielectric data shown in Figures 17 - 19 for Nylon-11, Nylon-7 and PVF<sub>2</sub> samples, respectively.

**Figure 21.** The static values of the electromechanical coupling coefficient  $k_{31}$  of Nylon-11, Nylon-7 and PVF<sub>2</sub>.

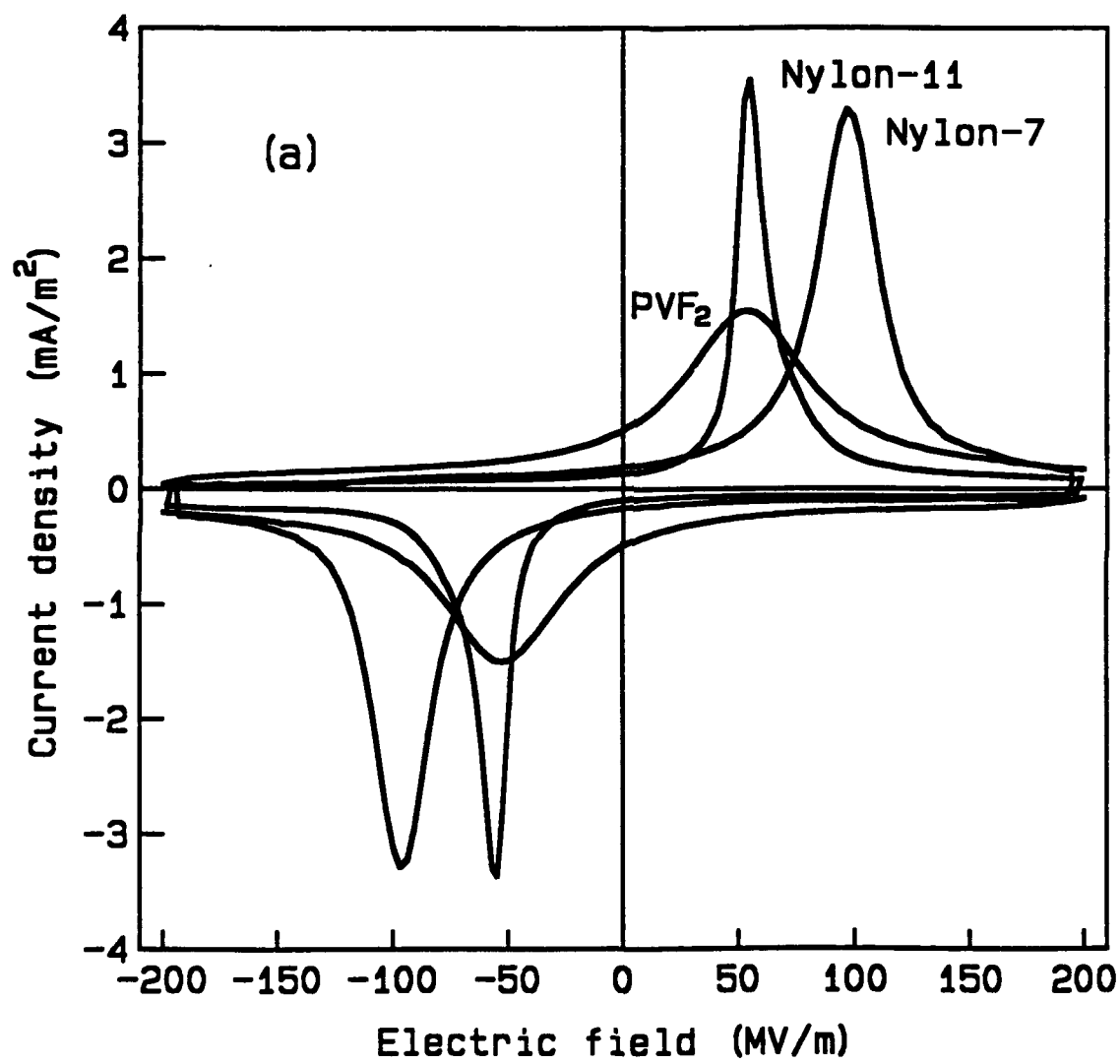


Figure 1 (a)

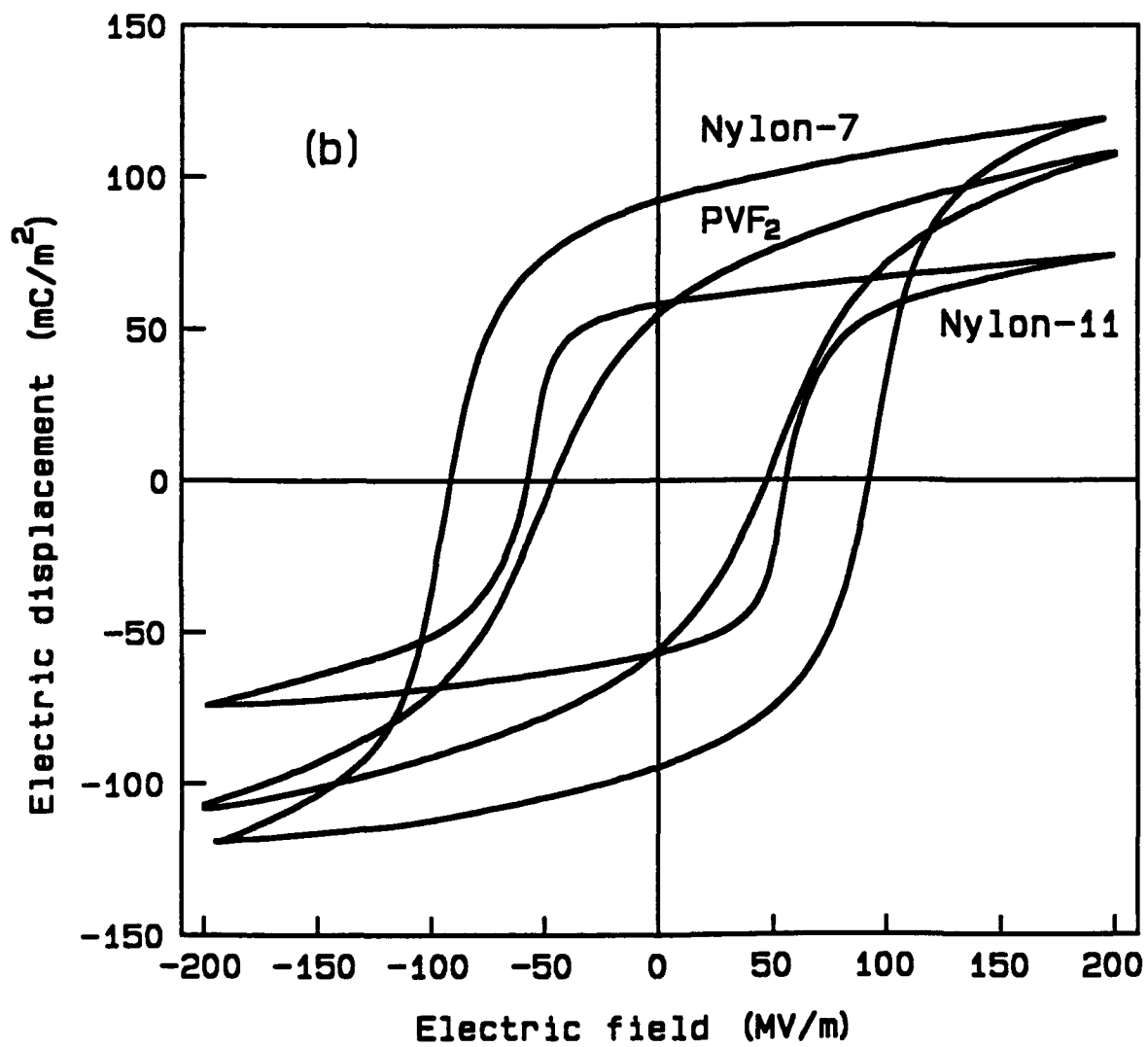


Figure 1 (b)

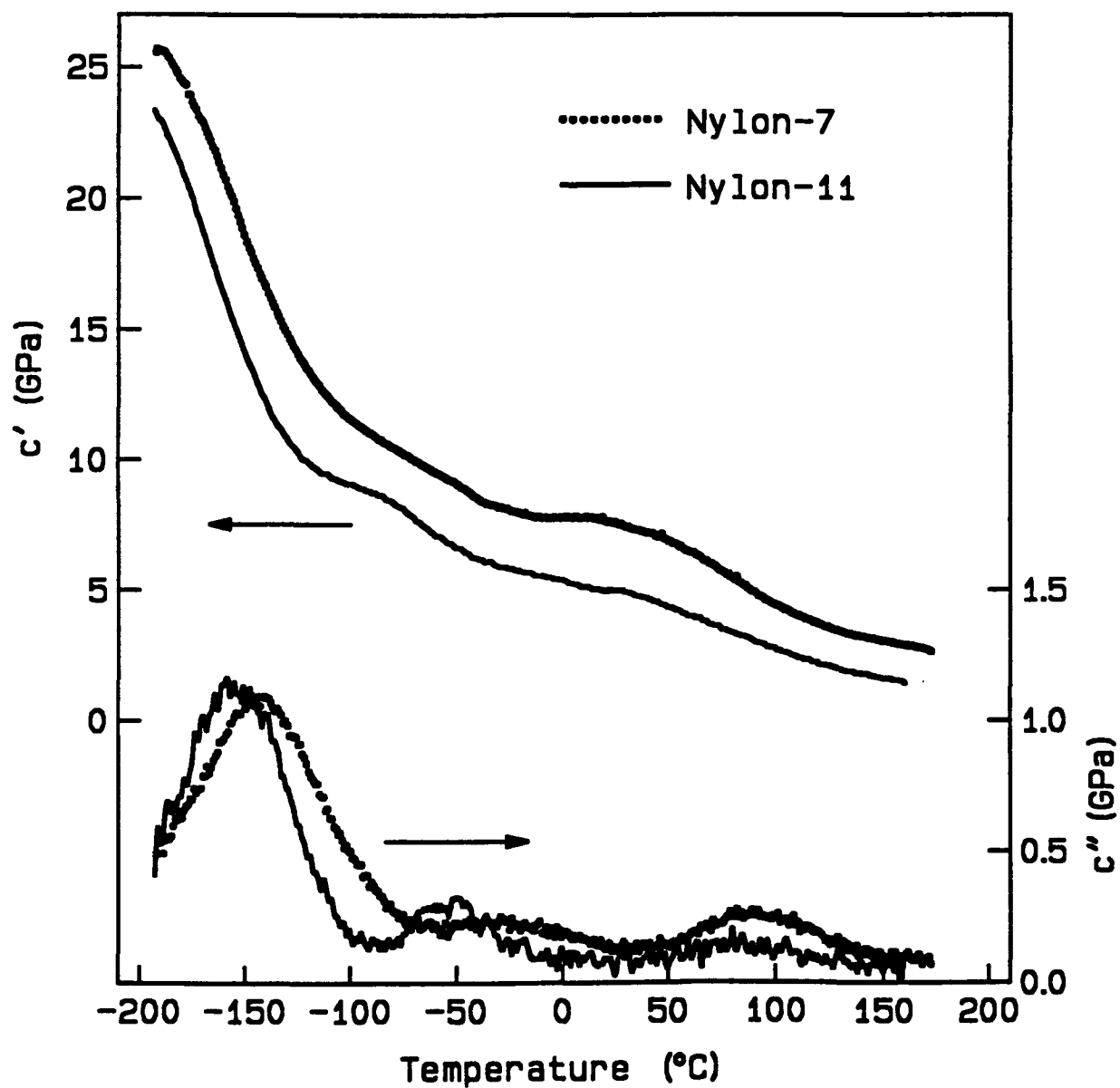


Figure 2

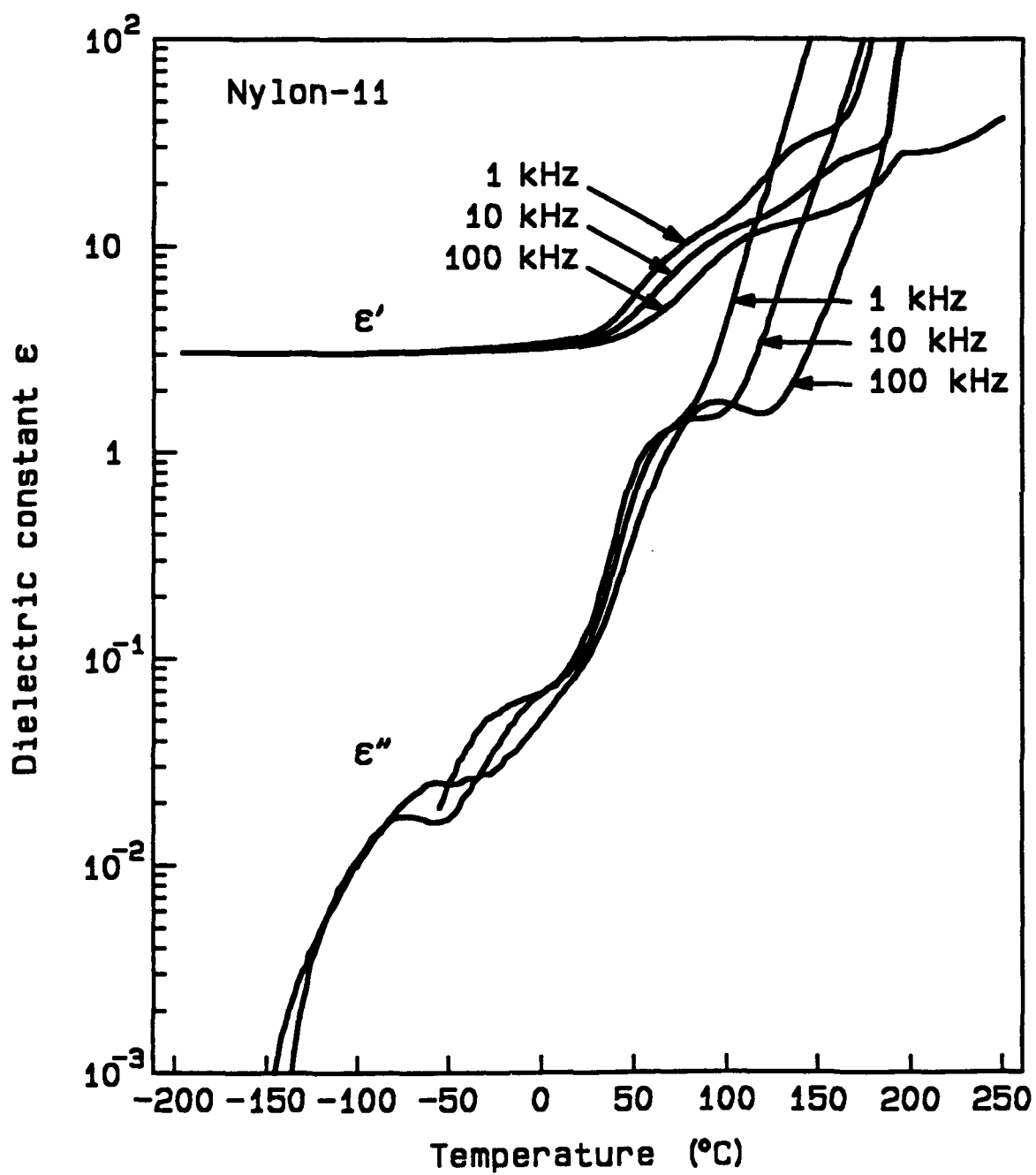


Figure 3



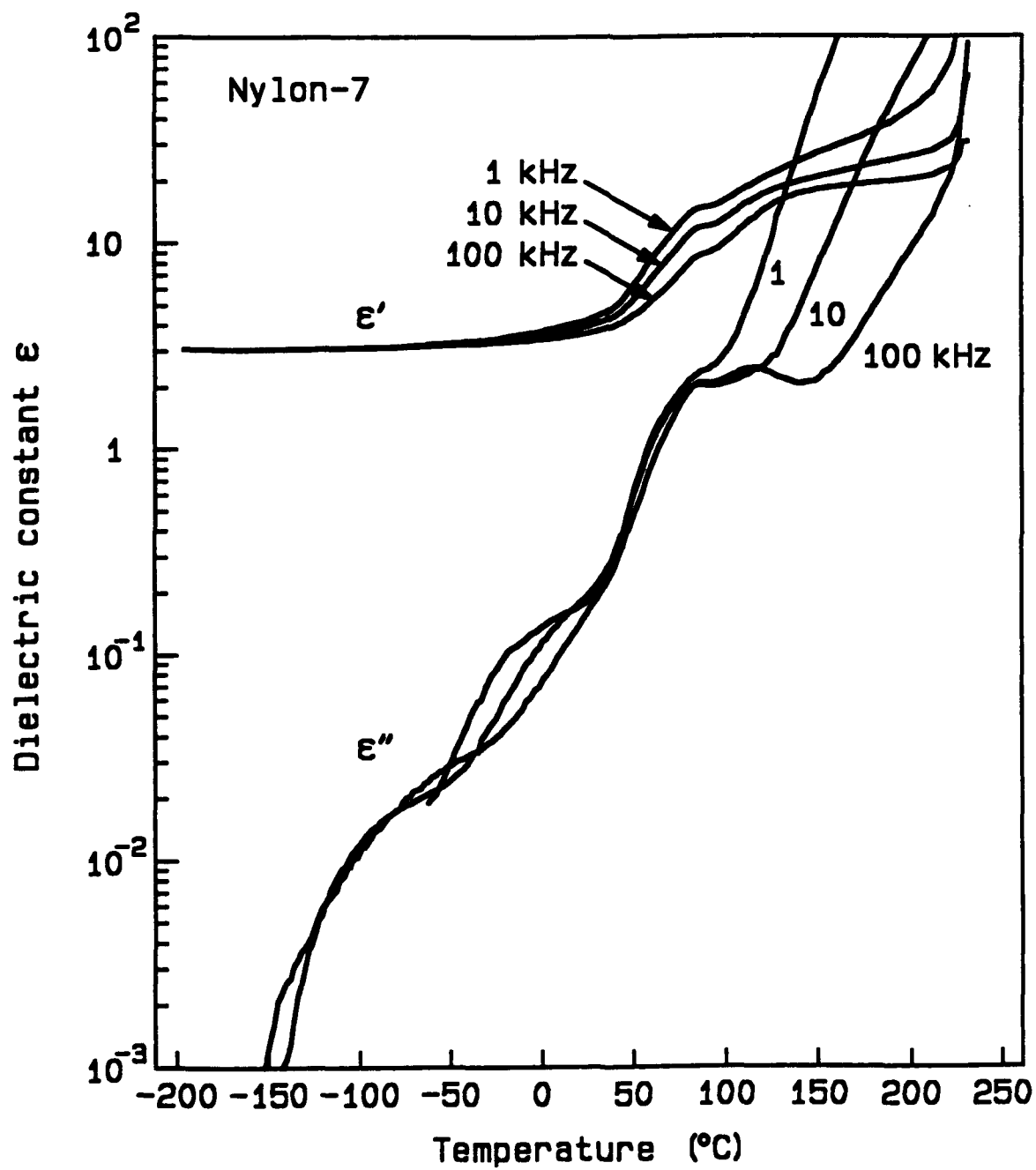


Figure 4

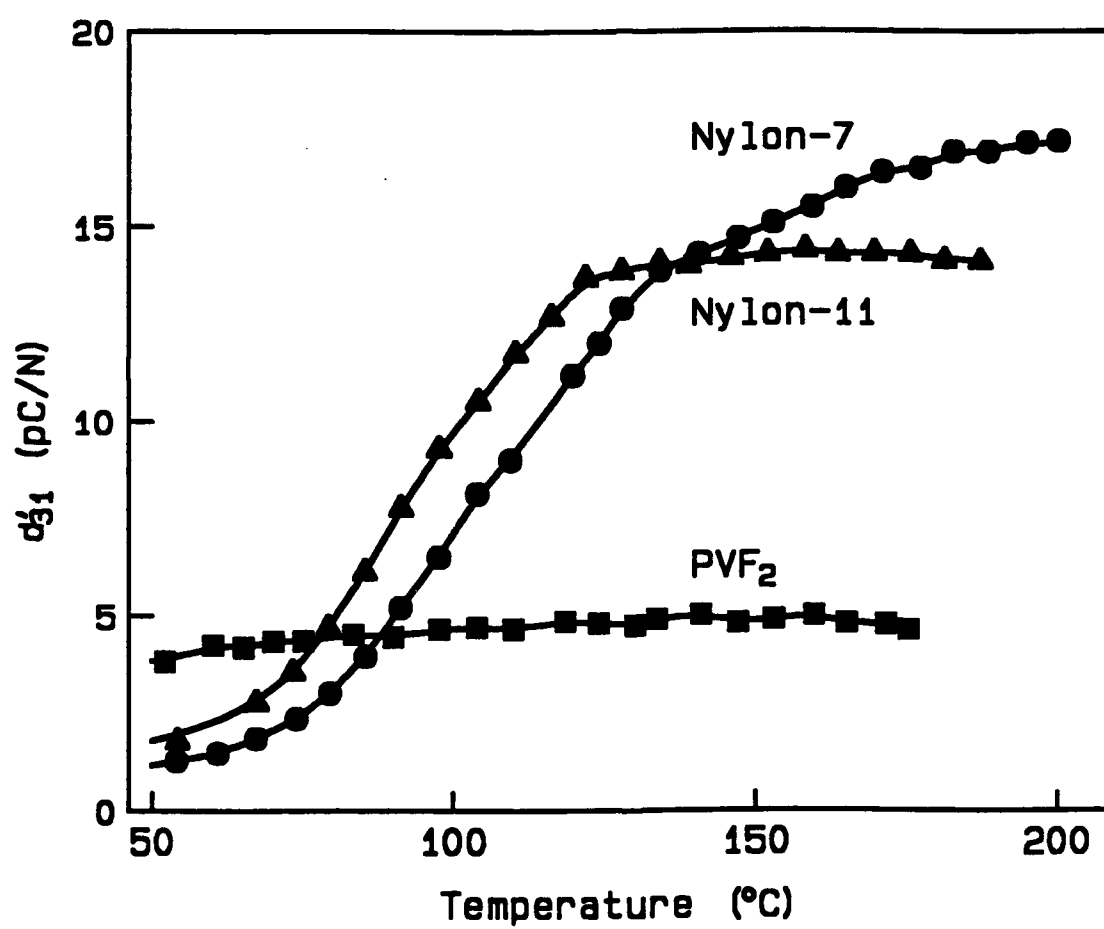


Figure 5

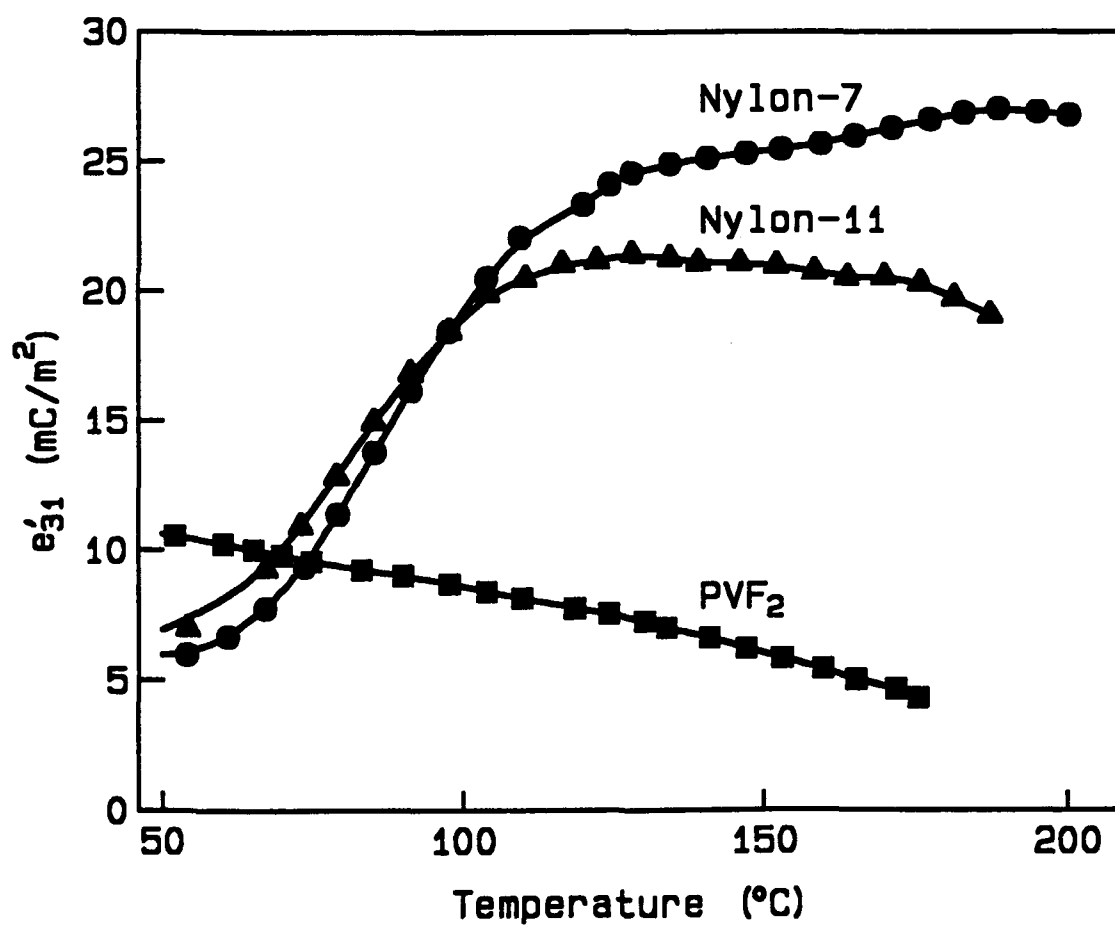


Figure 6

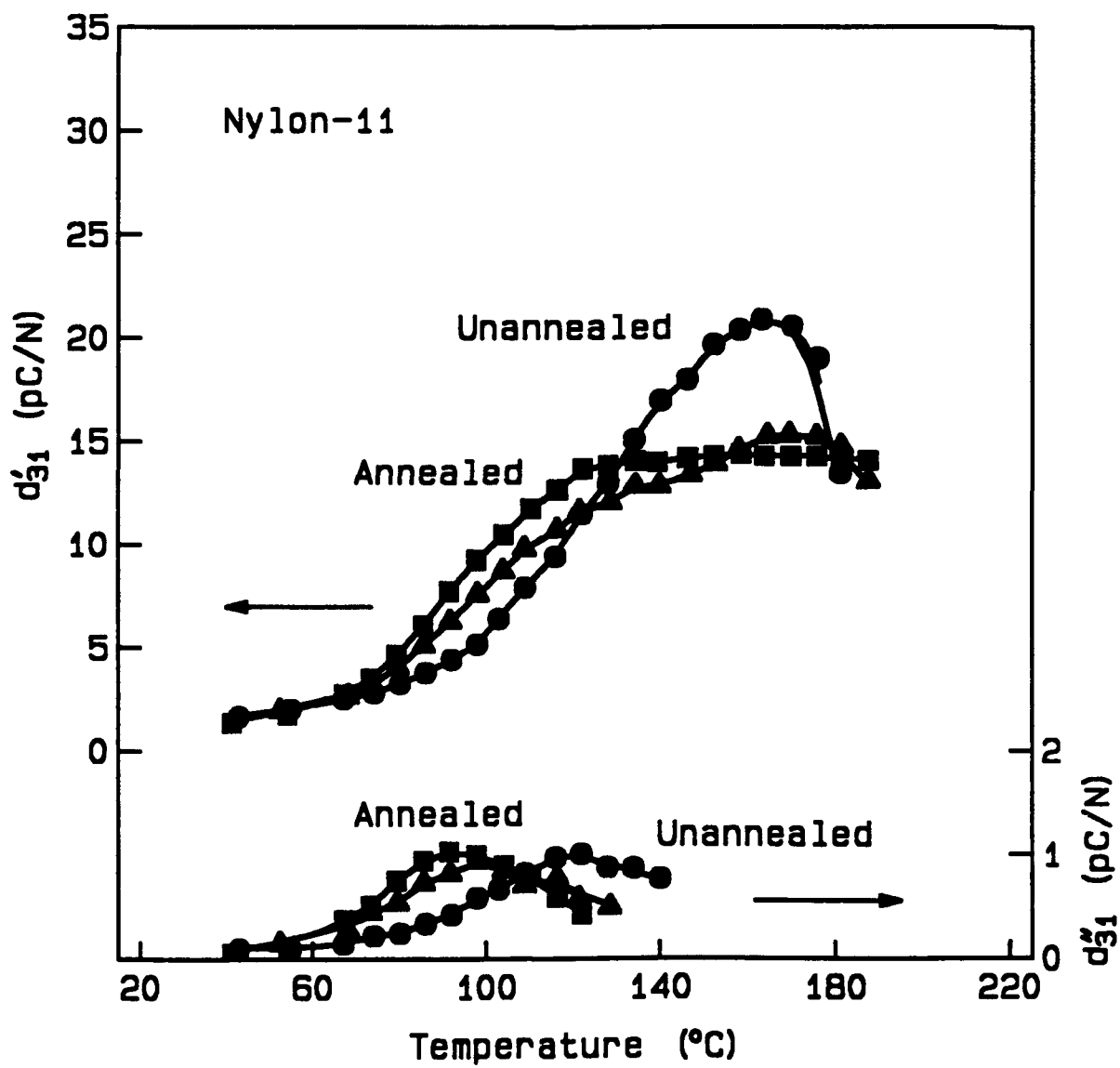


Figure 7

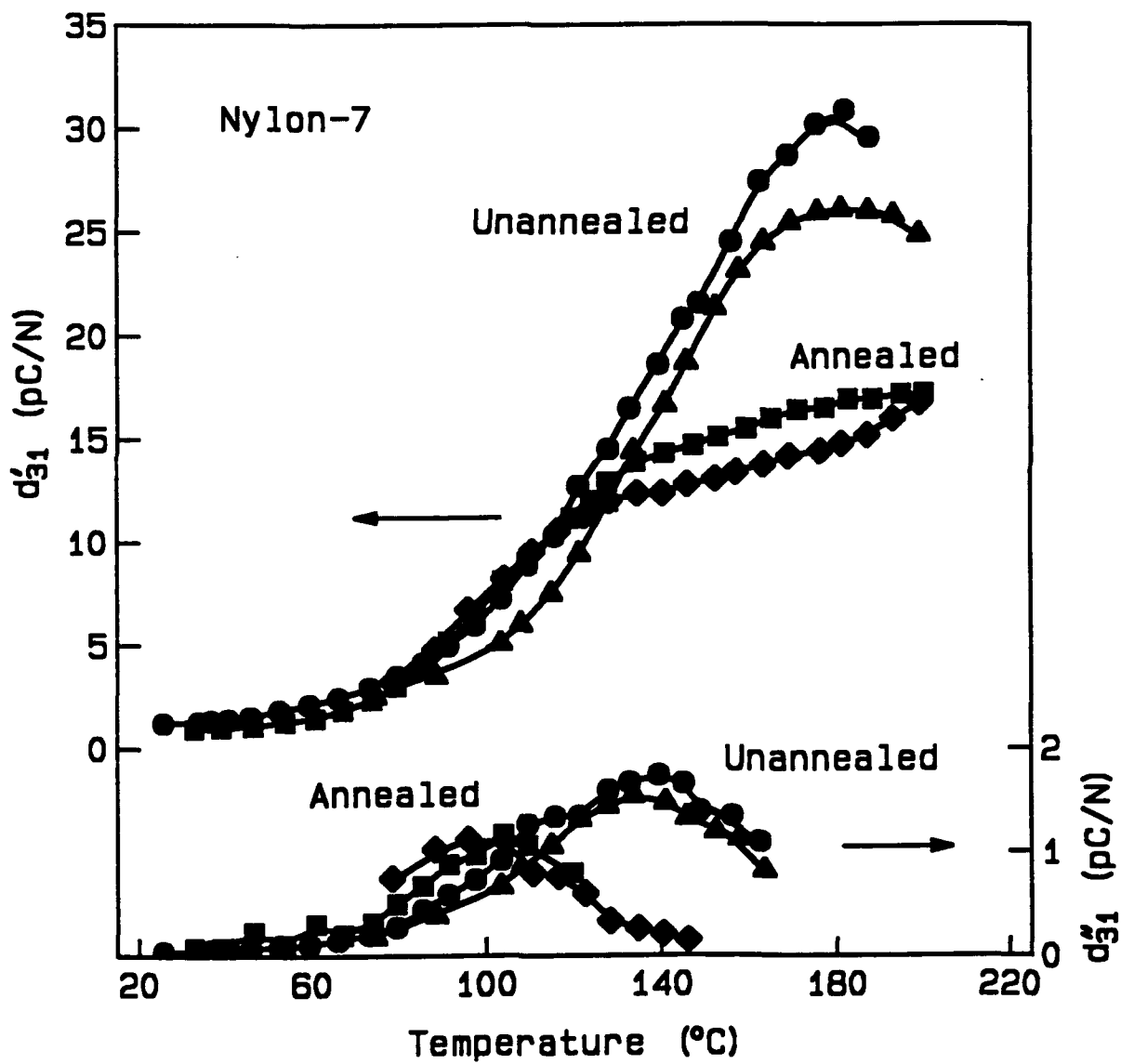


Figure 8

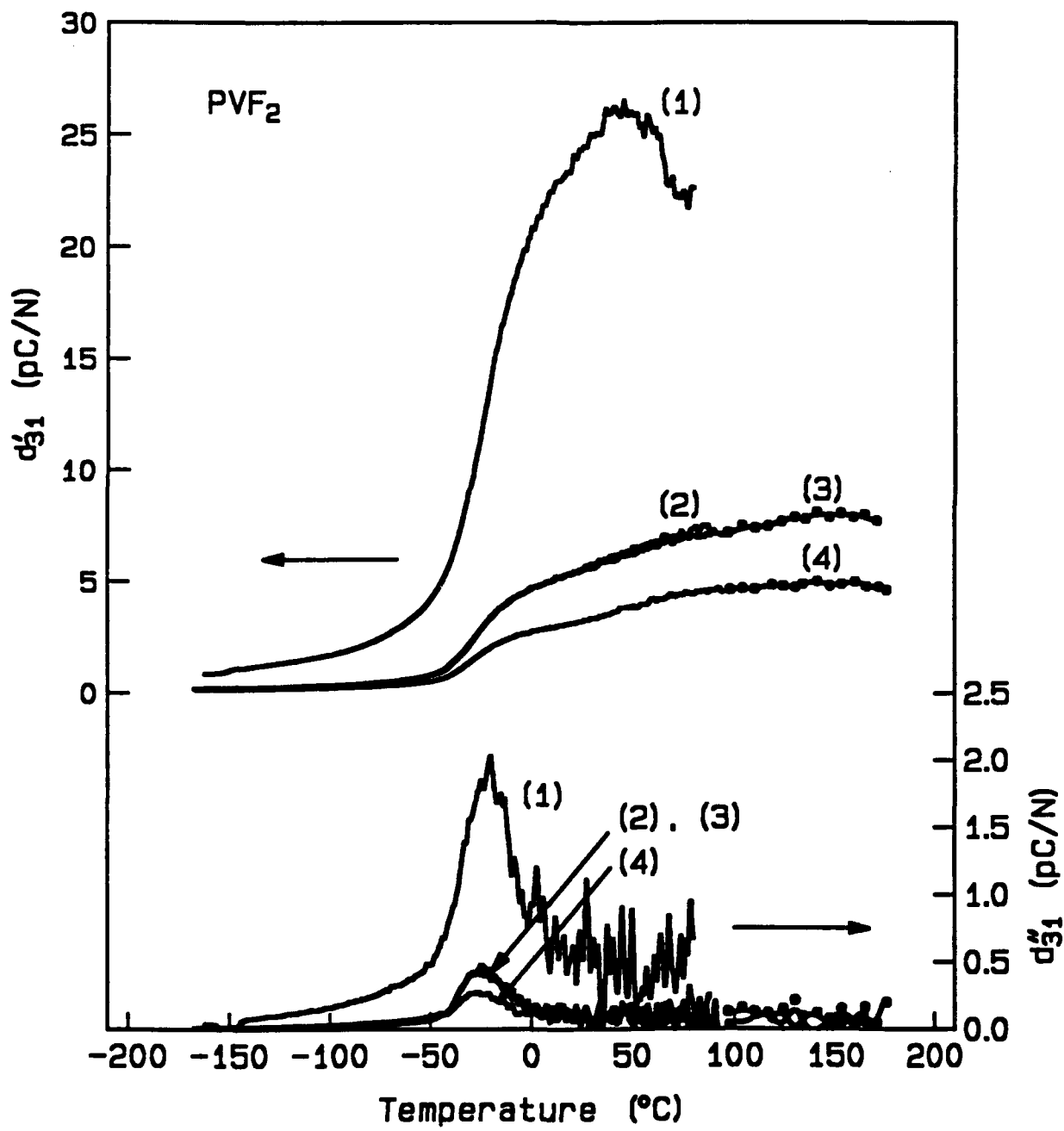


Figure 9

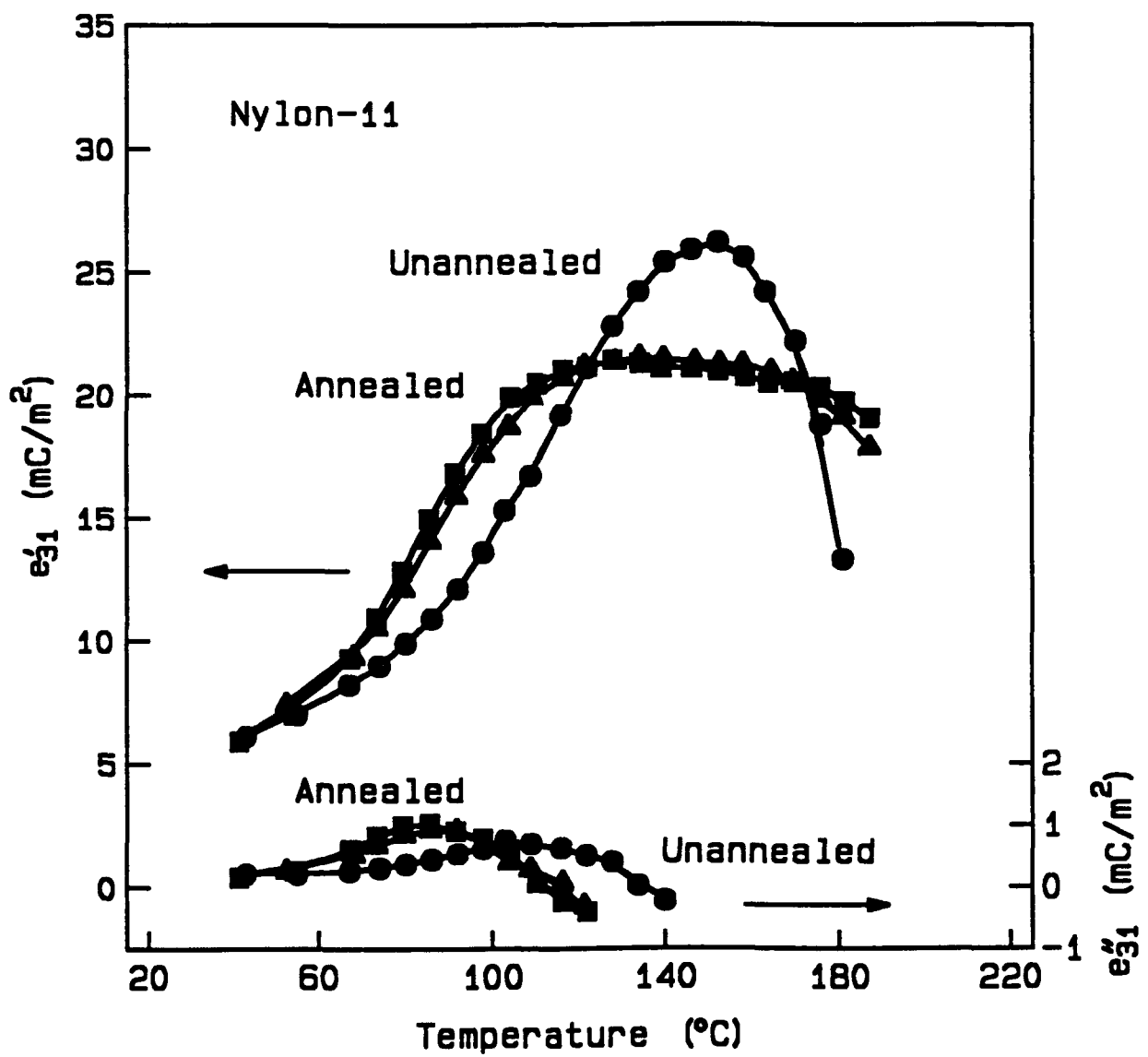


Figure 10

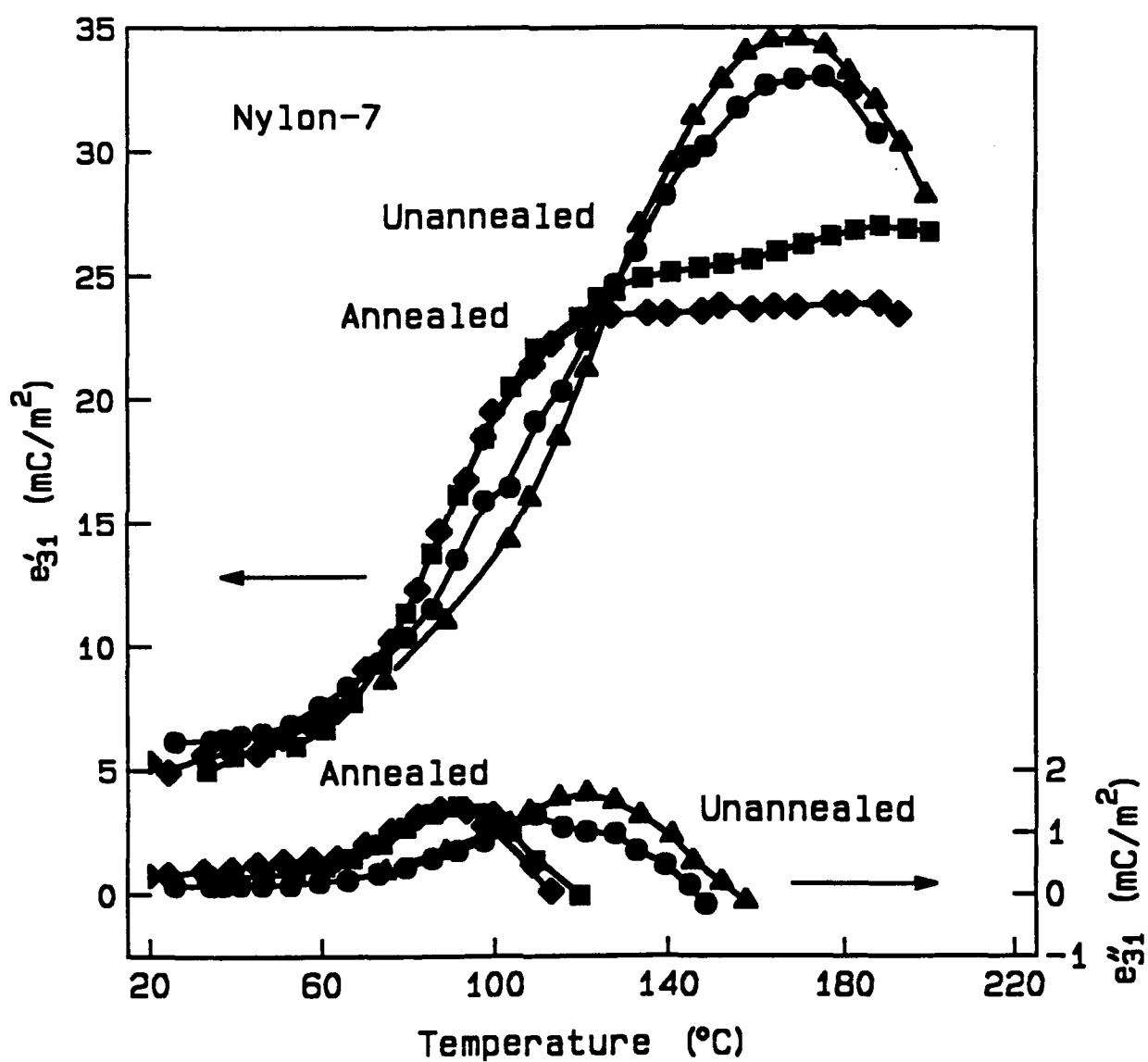


Figure 11



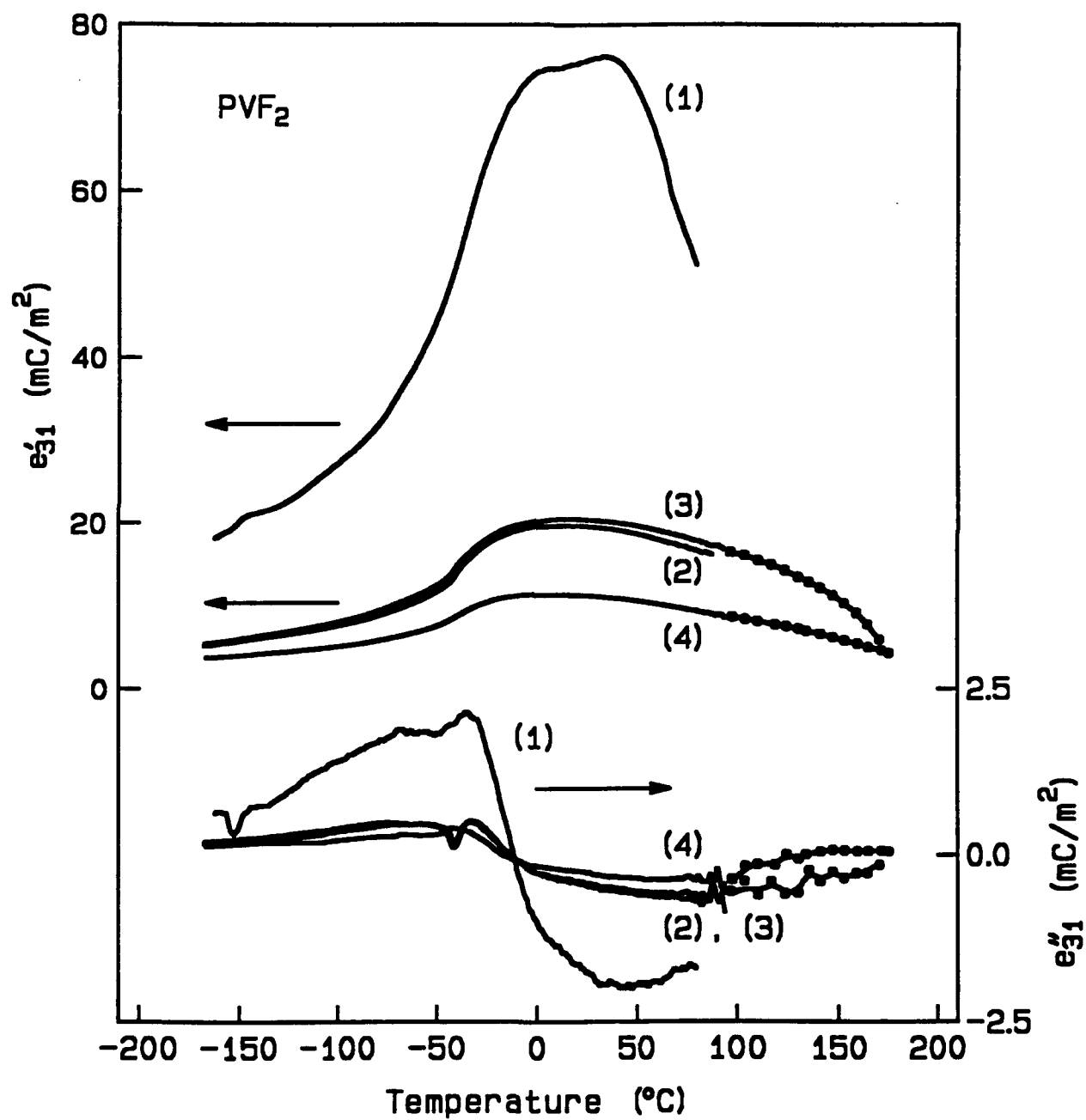


Figure 12

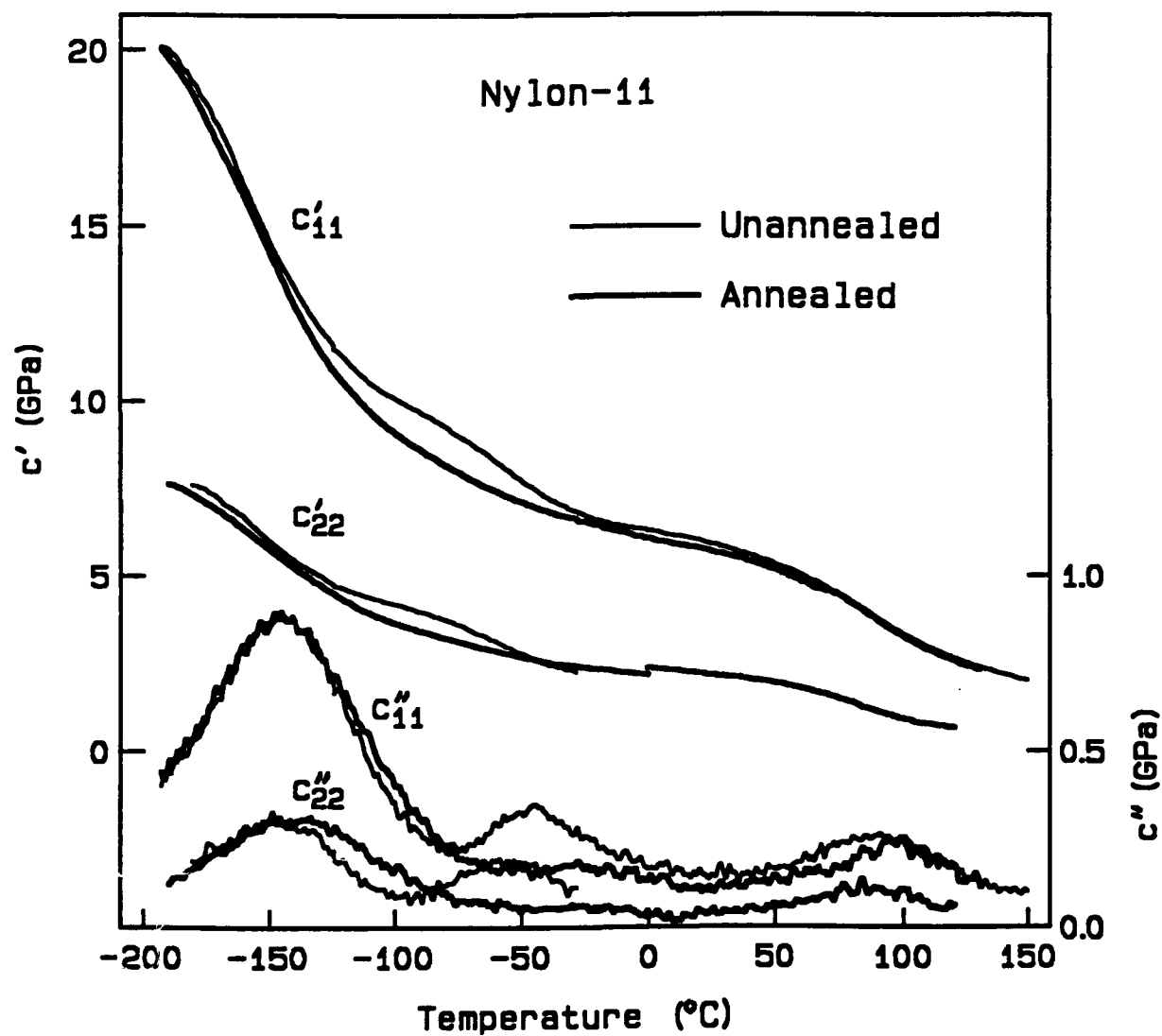


Figure 13

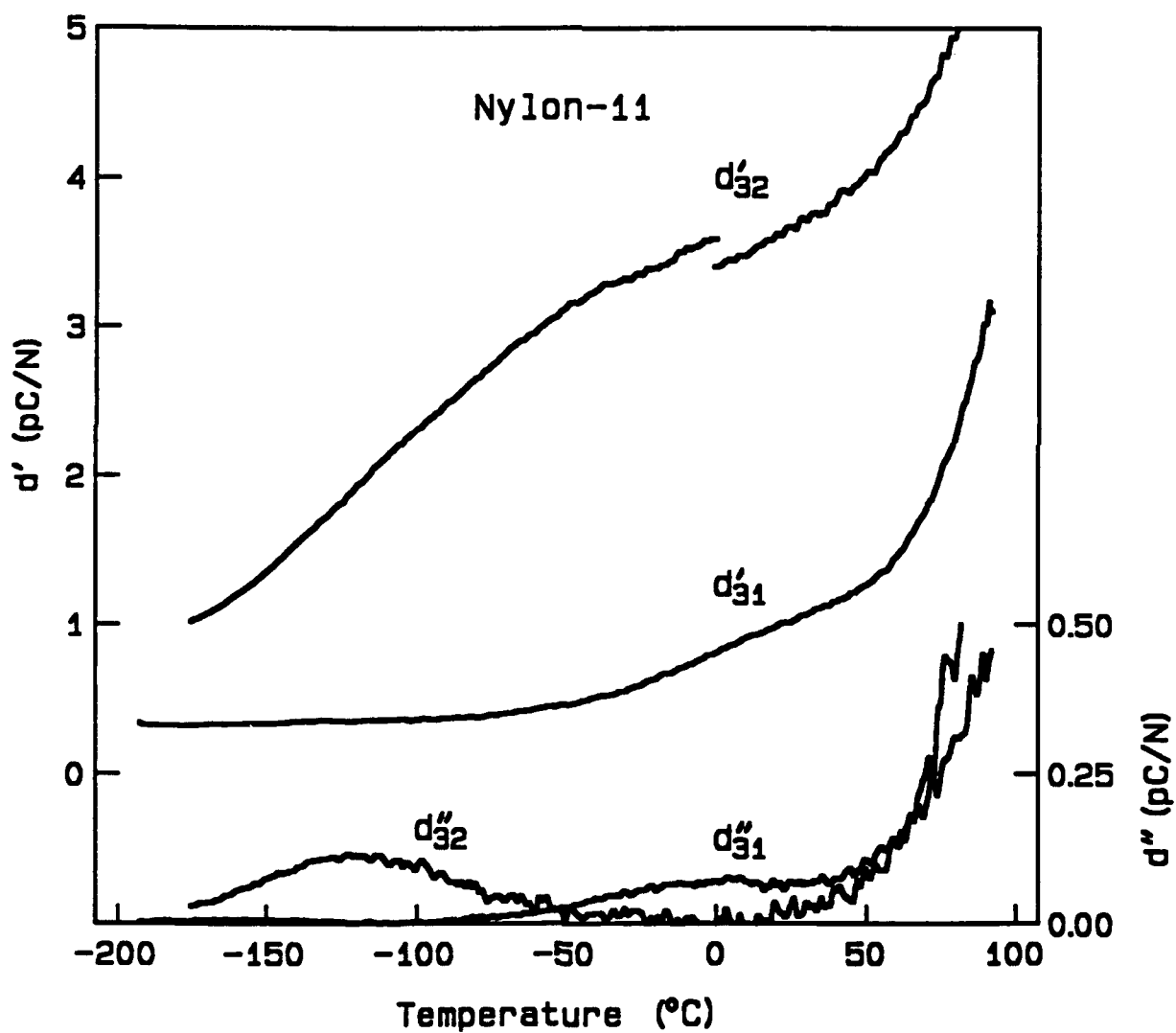


Figure 14

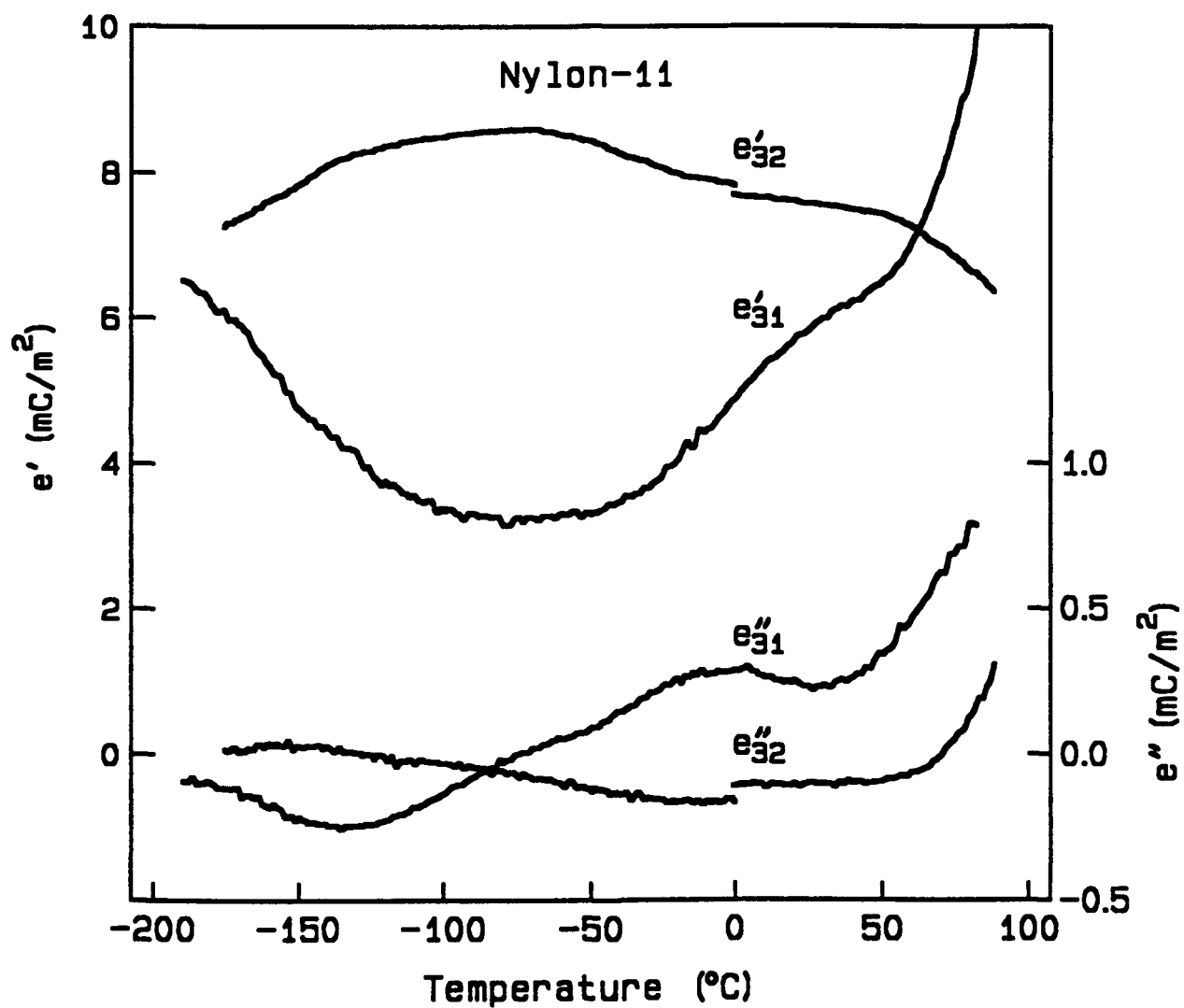


Figure 15

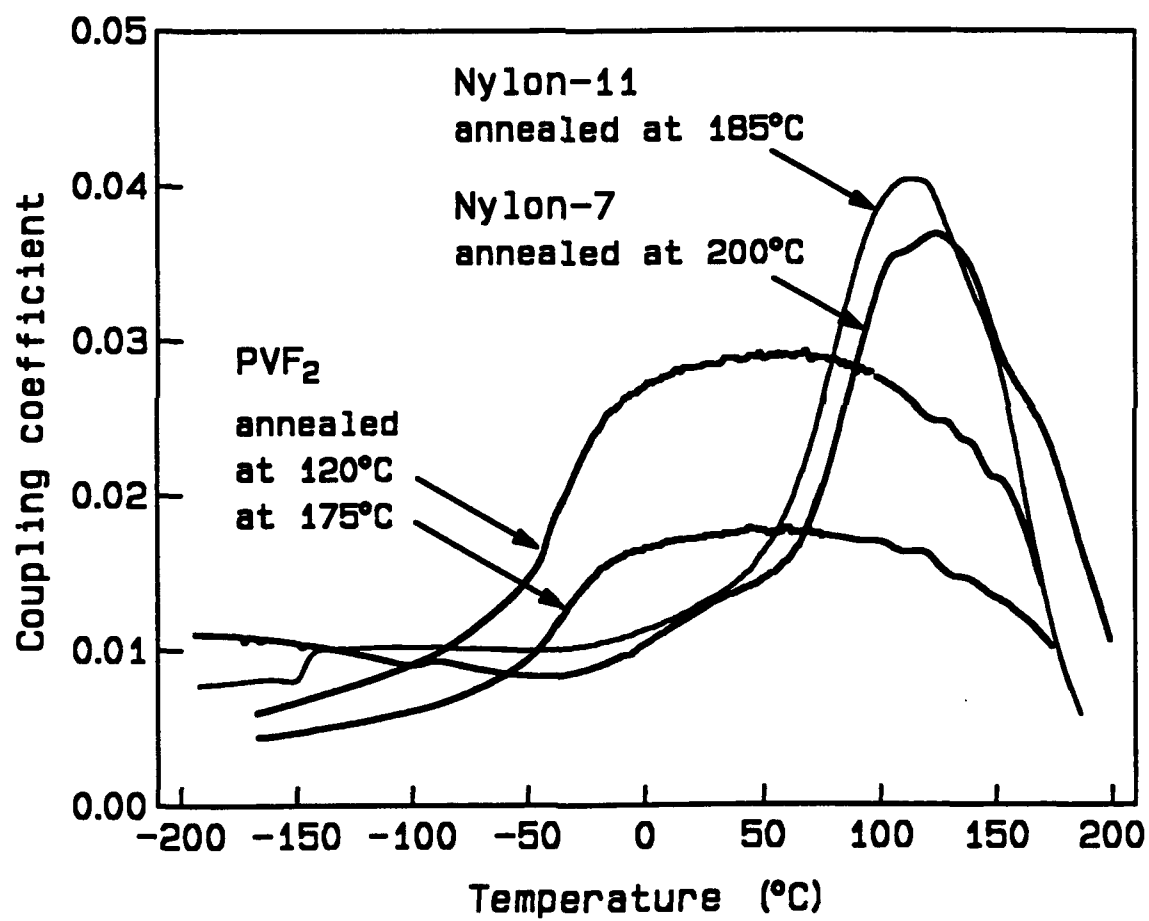


Figure 16

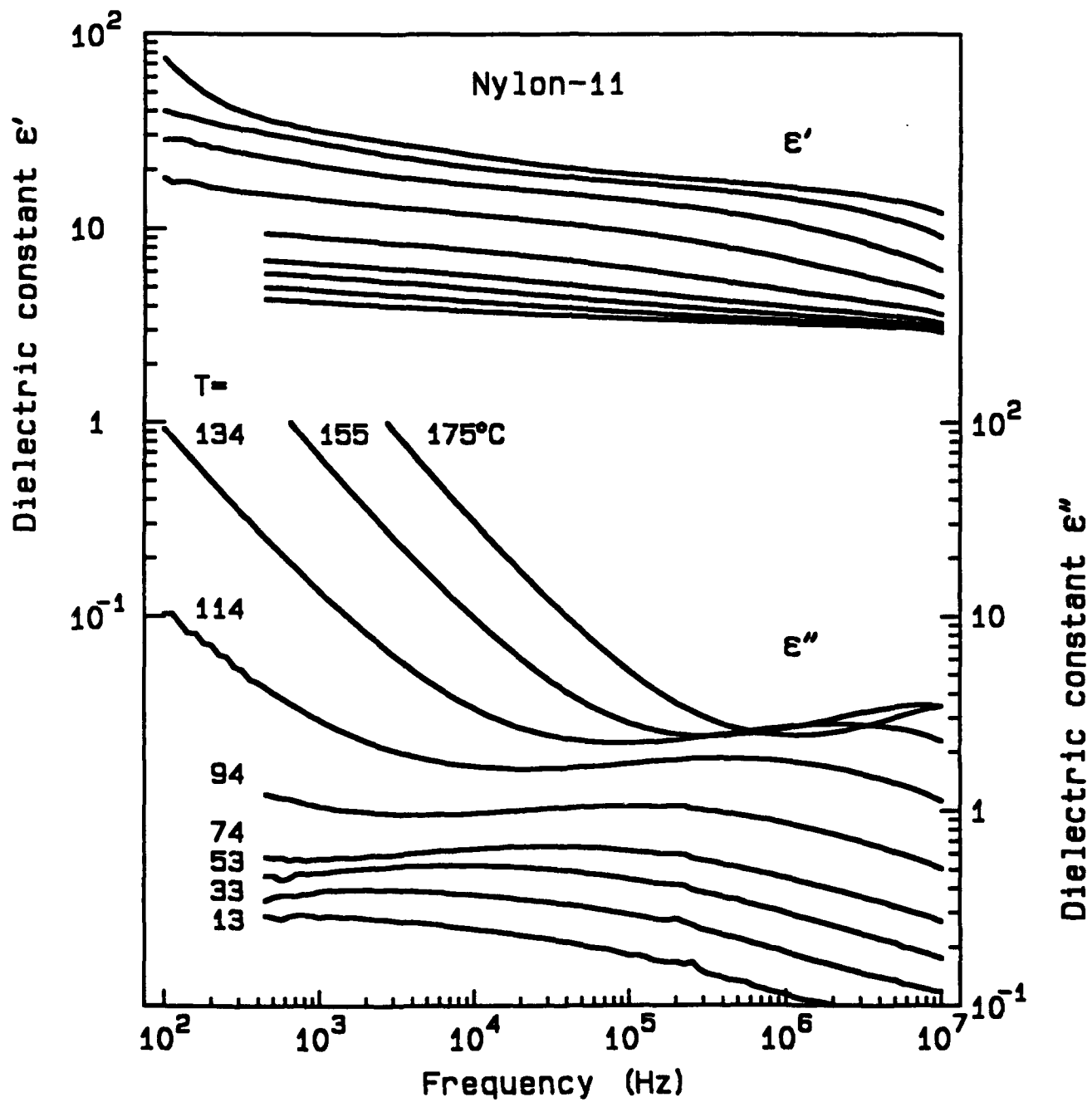


Figure 17

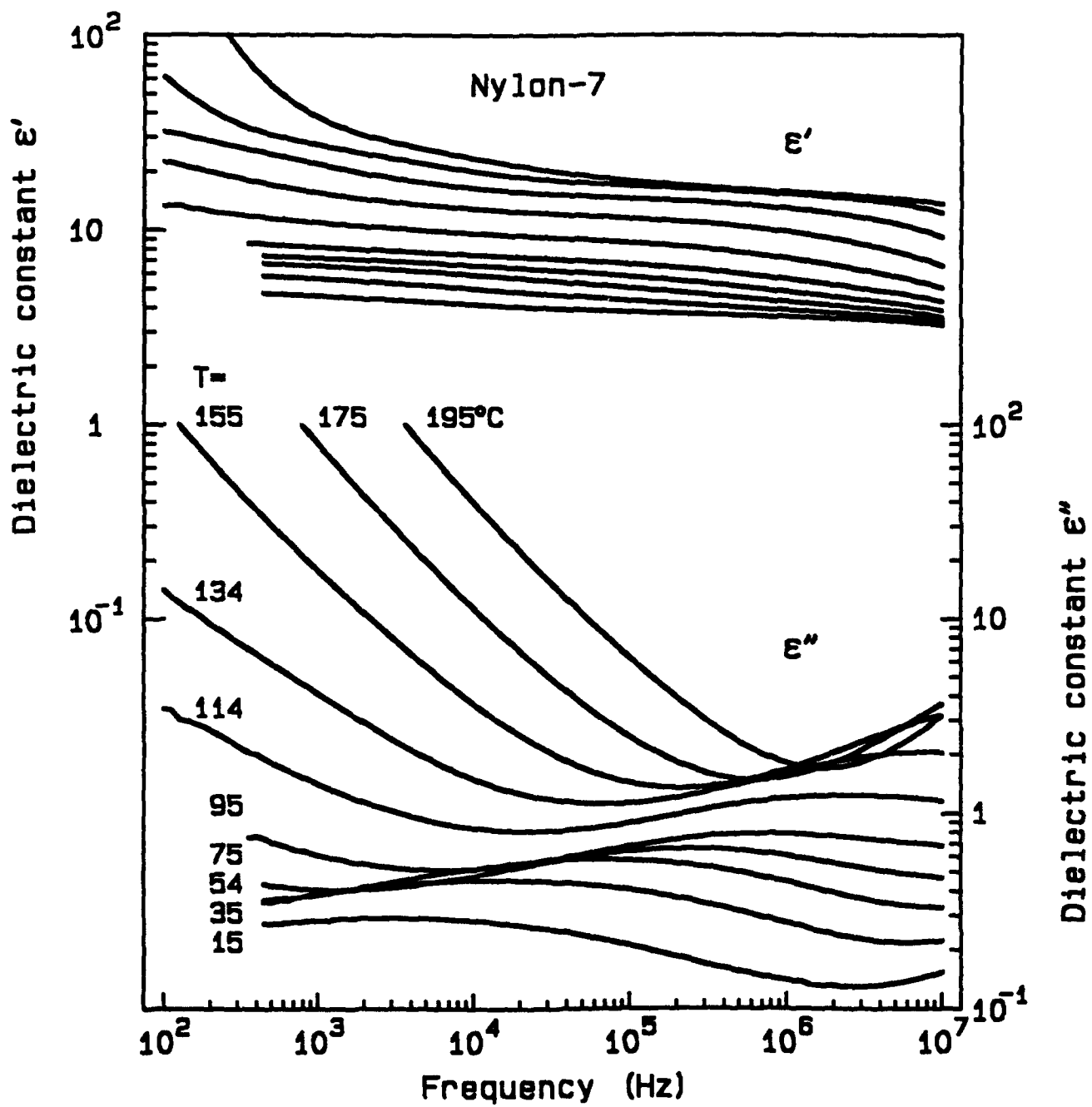


Figure 18

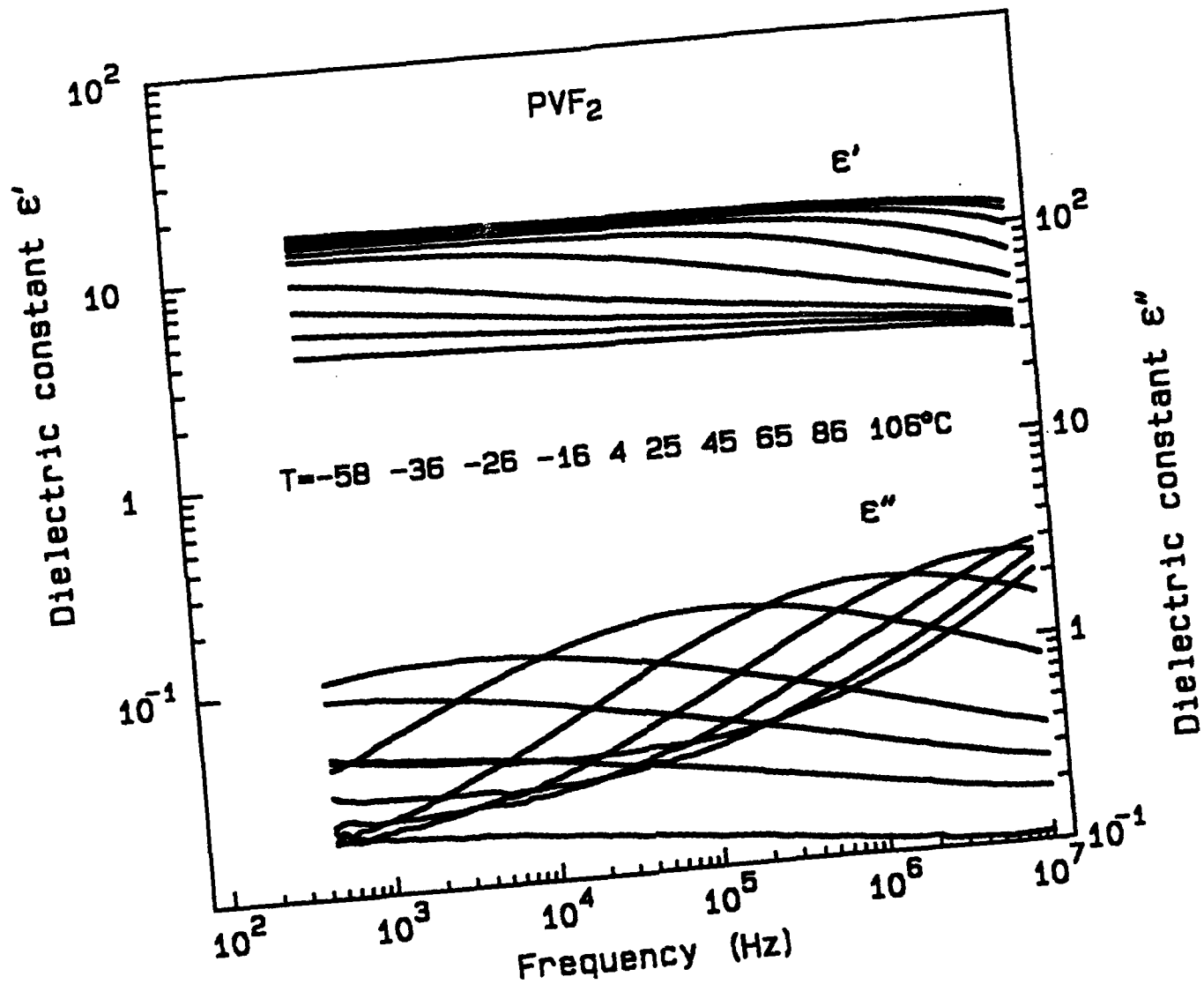


Figure 19



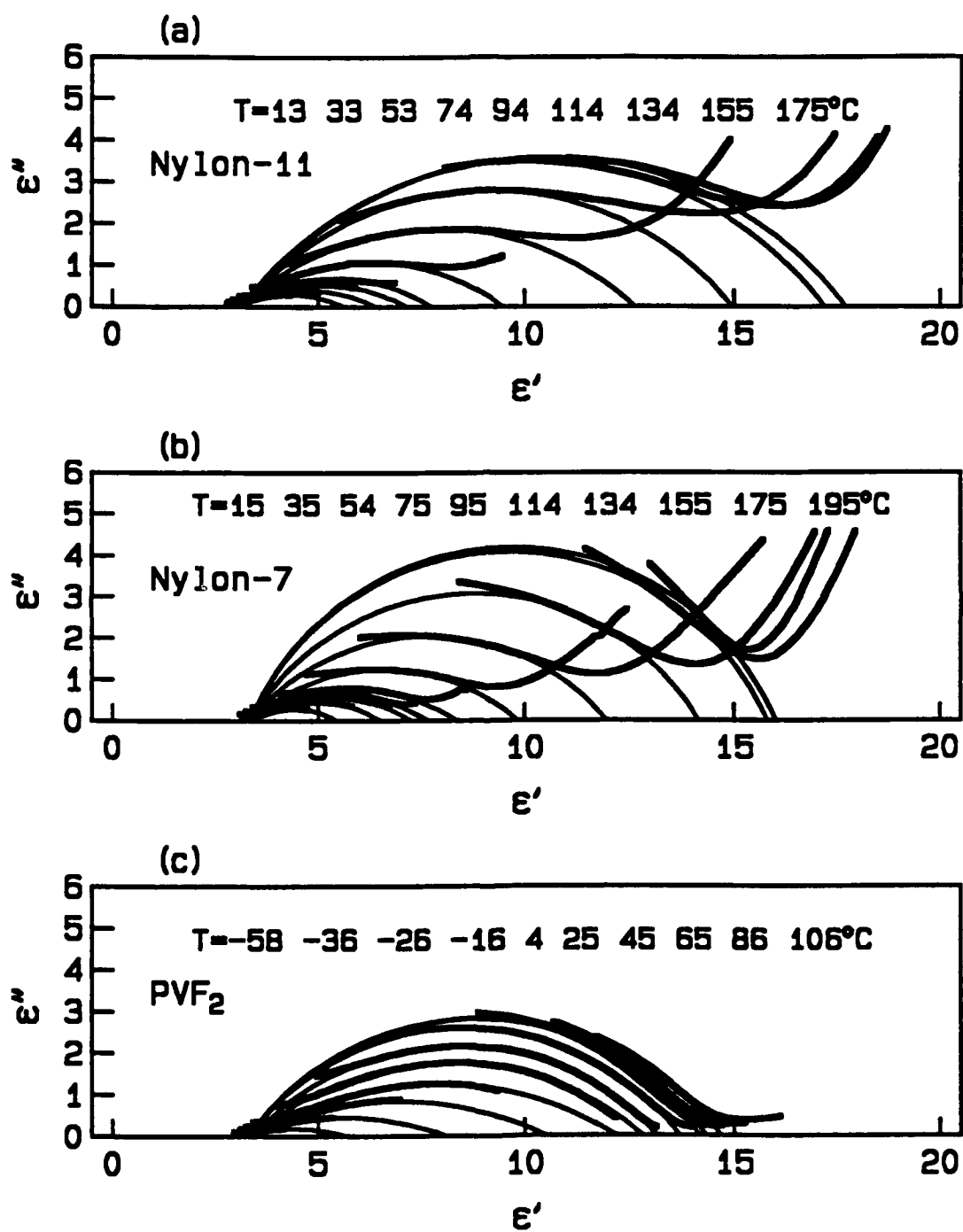


Figure 20

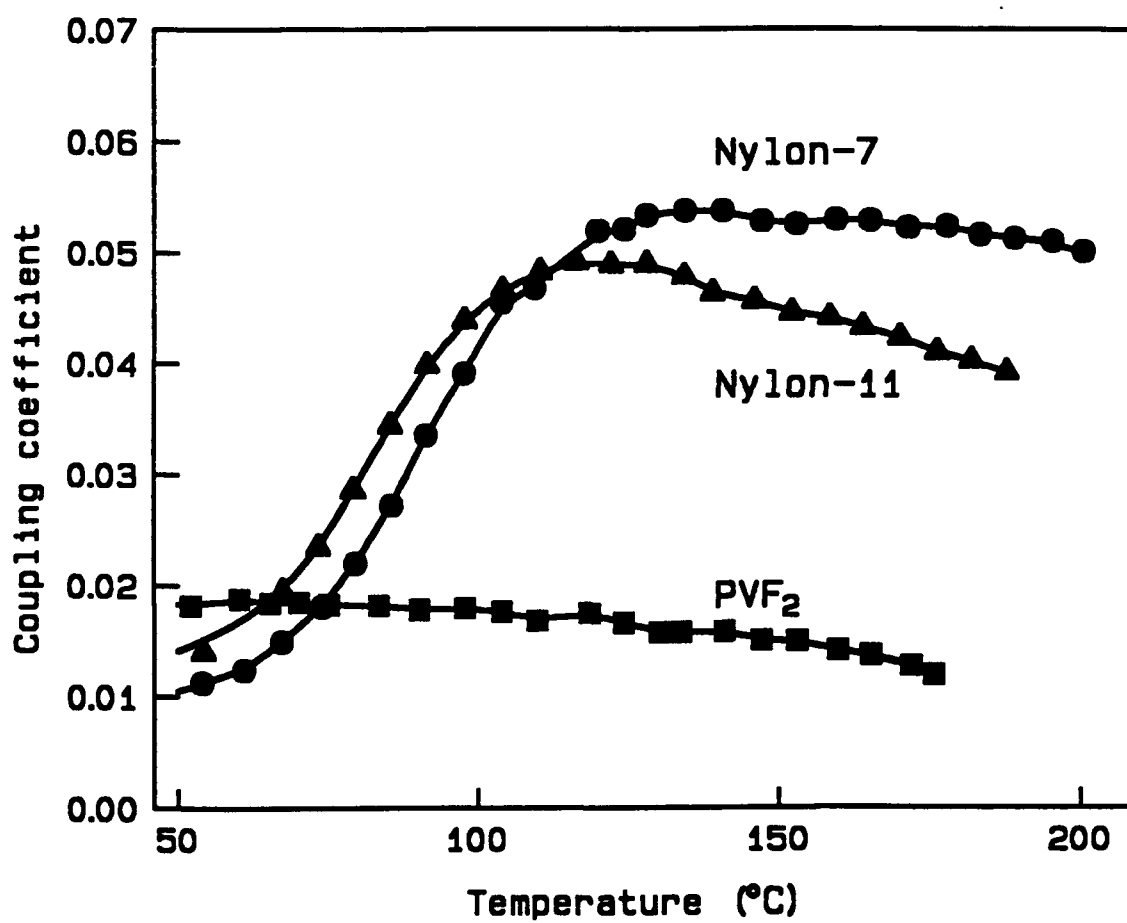


Figure 21